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TECHNOLOGY ASSESSMENT OF SELECTED HAZARDOUS WASTE MINIMIZATION PROCESS CHANGES

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The objective of this study was to technically evaluate selected industrial process changes for applications to Air Logistics Centers for hazardous waste minimization. Those processes evaluated were as follows: (a) Ion vapor deposition of aluminum as a replacement for cadmium electroplating, (b) Noncyanide strippers to replace cyanide strippers, (c) Plasma spray of chromium to replace chromium electroplating, and (d) Nickel boron as a replacement for chromium electroplating. The study resulted in the recommendation to develop databases, test plans, pilot studies, and demonstrations of the effectiveness of processes a and b, above, in minimizing hazardous waste generation. Processes c and d showed minimum potential for hazardous waste minimization, and were not recommended for further study.

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PREFACE

This report was prepared by the Air Force Engineering and Services Center,(AFESC) Air Force Engineering and Services Laboratory, (ESL), Tyndall Air Force Base, Florida 32403-6001. Mr. Charles J. Carpenter was the Government technical program manager. This report summarizes work accomplished between 30 September 1986 and 30 April 1987.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). A NTIS it will be available to the general public, including foreign nations.

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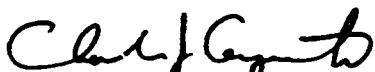
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A. OBJECTIVE

The PACER IMPACT meeting of April 1986, at Tyndall Air Force Base,
Florida, requested Headquarters, Air Force Engineering and Services Center,
Environmental Sciences Branch (HQ AFESC/RDVW) investigate the possibilities
of the following: (1) Ion vapor deposition of aluminum to replace cadmium
plating, (2) Noncyanide strippers to replace cyanide strippers, (3) Plasma
spray to replace some chromium plating, and (4) Nickel boron to replace some
chromium plating. These process changes would fall under the category of
waste reduction, reducing or eliminating cadmium, chromium, and cyanide from
the electroplating shop, and, at the same time, enhance productivity. This
report provides recommendations on the initial findings from the suggested
lines of investigation.

PACER IMPACT, an MA-sponsored program, includes five groups. One of
those is the Environmental Development Group (EDG). The EDG focus is to
enhance productivity through looking at industrial processes from an
environmental perspective, create a forum for crossfeeding specific
initiatives between ALCs, and ensure a method of traceability for produc-
tivity enhancements in the environmental arena. This program is in response
to the presidential mandate to increase productivity by 70 percent by 1992.

B. BACKGROUND

For nearly 80 years, our air forces have been making technological leaps,
from Wright-supplied machines, through the F-15, F-16, B-1B, and SR-71.
These advancements have greatly expanded our knowledge of science and
environment and are supported by research, development, acquisition,
provisioning, depot repair, and other support activities, which take an
increasing proportion of the national defense dollar.

Because of legislative and legal pressures, past problems have become
important enough to dictate future policy. Environmental problems are
within this category. All modern weapons systems, with their extensive
maintenance programs, produce large quantities of hazardous wastes. The
Department of Defense (DOD) disposes of 675,000 metric tons of hazardous
wastes per year. Of this, the Air Force produces 47 percent and the Air
Logistics Centers contribute about 75 percent (Reference 1). Cost of
disposal can be over $137 per ton. In FY 87, $327 million were allocated
for the Defense Environmental Restoration Program (DERP). An estimated $2
billion is required for cleanup of old hazardous waste sites for improved
waste treatment, fines, disposal, research, civil engineering, etc., and
management of hazardous wastes. (This value increases each year with
economic pressures forcing focus on only the most pressing of the
problems.) To avoid creating these economically draining problems, we
cannot ignore problems until they become critical; but we must eliminate
them before they start. This will require the coordinated efforts of those
who shape operational doctrine and strategy and those who formulate our
research and development (R&D) programs.

The OTA has recently provided official support for reduction practices. Combined federal and state spending on pollution control amounts to $16 billion annually, but only $4 million of this goes to reduction practices. Use of manufacturing waste reduction practices, such as changing raw materials, operational procedures, or end products, should have primacy over waste treatment or disposal technologies. The OTA estimates that much less than 50 percent of EPA's funding for "waste minimization" R&D applies to waste reduction, even though the agency has identified waste reduction as one of two categories of waste minimization. (Waste reduction has become a minor tool of alternatives to land disposal.) The Air Force must not follow this pattern.

C. APPROACH

Waste reduction is the practical solution. Waste reduction, as defined by OTA, is "in-plant practices that reduce, avoid, or eliminate the generation of hazardous waste so as to reduce risks to health and environment." This is as opposed to "end-of-pipe" hazardous waste management, with hazardous waste defined as "all nonproductive hazardous outputs from an industrial operation into an environmental media, even though they may be within permitted or licensed limits."

Waste reduction avoids waste management liabilities. Waste reduction should be the first option of generators because all waste treatment and recycling facilities pose some environmental risks, thus requiring effective regulation. About 10 percent of superfund sites on the current national priorities list are a result of mismanagement or technological failure at recycling or waste treatment plants. The most certain means of preventing environmental risk is through waste reduction.

DEFINITION OF PROBLEM

A. POLLUTION CONTROL REGULATIONS FOR ELECTROPLATING

The electroplating industry is bound by a multitude of federal pollution control requirements for wastewater and solid waste residues. The US Environmental Protection Agency (EPA) is responsible for preparing the detailed regulations and establishing the administrative compliance procedures.

The environmental legislation, affecting water pollution control and waste management in the electroplating industry, is summarized in Table 1. Before 1972, water pollution control requirements were established by the individual states, and were based primarily on "water body usage."

TABLE 1. ENVIRONMENTAL LEGISLATIVE ACTIVITY AFFECTING ELECTROPLATING

Year	Legislation	Requirements
1972	Federal Water Pollution Control Act (FWPCA) Amendments (PL 92-500)	Required all industrial discharges into waterways must meet technology-based standards of pollution control. Best practicable technology (BPT) by 1 Jul 77. Best available technology (BAT) by 1983 (later revised to 1984). New source performance standards (NSPS). If source begins construction after publication of the applicable proposed regulations. Required all industrial municipal discharges to attain industry-specific effluent limitations (pretreatment standards). Required periodic review and updating of technology-based requirements. Established National Pollutant Discharge Elimination System (NPDES) permit program. Required self-monitoring program. Established federal control over municipal systems.
1976	National Resource Defense Council (NRDC) Consent Decree (NRDC et al. vs Train)	Committed EPA to a schedule for developing BAT effluent limitations for 21 major industries, including electroplating, covering 65 recognized toxic substance classes. This schedule was later incorporated into the Clean Water Act.
	Resource Conservation and Recovery Act (RCRA) (PL 94-580)	Established controls for disposal of all solid wastes. Defined hazardous solid waste and

Year	Legislation	Requirements
		established tests to determine which wastes are covered. Established standards for solid waste generators, storage facilities, and disposal sites. Established manifest system for transportation of hazardous waste.
1977	Clean Water Act (PL 92-217)	As an amendment to FWPCA, revised FWPCA deadlines. Defined classes of pollutants as toxic, conventional, and nonconventional with major emphasis on the toxic compounds associated with the NRDC consent decree. Linked pretreatment standards to BAT guidelines for toxics. Established BCT (best conventional technology) level of compliance for industrial discharges of conventional pollutants (e.g., oil and grease, pH, suspended solids, biochemical oxygen demand) based on the cost to municipalities to treat conventional pollutants and industries' incremental treatment costs. Authorized municipal systems to relax pretreatment standards under certain conditions for individual dischargers.
1984	Hazardous and Solid Waste Amendments of 1984 (PL 98-616)	As an amendment to RCRA, brought small quantity generators ($100 to $1,000K per month) under RCRA. Manifests became necessary, 180-day onsite storage. Required certification of generators after 1 Sep 85, showing generation of hazardous waste was minimized. Required that new underground storage tanks be constructed to prevent leaks, and existing tanks monitored. Prohibited landfilling of bulk or noncontainerized liquids after 8 May 85. Banned certain wastes from land disposal unless demonstrated not harmful. Required certain surface impounds receiving hazardous wastes to be retrofitted with double liners, groundwater monitoring capabilities, and leachate collection systems.

Year	Legislation	Requirements
		Required EPA to report to Congress on hazardous wastes not addressed by RCRA because they are sent through municipal sewers.

EPA has prepared a number of regulations to provide specific guidance for carrying out the requirements of the legislation. These regulations contain achievable specific performance standards for processes ar contaminants.

Wastewater regulations, including enforcement mechanisms, have been divided into several layers of categories: those for existing sources and new sources; and those for direct and indirect dischargers. Direct dischargers are regulated by NPDES, under which EPA or its state equivalent issues a separate permit to each discharger. This permit contains specific discharge limitations, reporting requirements, and compliance schedules. Indirect dischargers must conform to national pretreatment standards, which are enforced by the local government under EPA.

For regulating purposes, electroplating plants have been divided further into several categories. Facilities are first divided into captive or job shops, then into integrated or nonintegrated plants. A captive shop owns more than 50 percent of the area of materials undergoing metal finishing, and a job shop less than 50 percent. An integrated facility combines electroplating waste streams with other waste streams, and a nonintegrated facility does not. The electroplating and metal finishing water pollution control regulations are contained in the US Code of Federal Regulations (CFR) Title 40, Parts 413 and 433, respectively. Table 2 contains effluent limitations for existing direct dischargers, existing indirect dischargers with metal finishing facilities, and new sources. Table 3 contains pretreatment standards for existing dischargers with indirect nonintegrated facilities.

The treatment of electroplating wastewater, as required by the National Pretreatment Standards or NPDES requirements, will result in an effluent that must comply with regulations for acceptable pollutant discharge and a residue (sludge) containing high concentrations of hazardous substances. Recent hazardous waste regulations have drastically altered the manner in which these materials are stored, treated, and disposed of. EPA regulates all aspects of management and control of all hazardous wastes from point of origin to final disposal. The regulations are a result of RCRA (PL 94-580) and the 1984 Hazardous and Solid Waste Amendments to RCRA (PL 98-618).

Under RCRA, solid wastes include all substances destined for disposal and not already regulated by the Clean Water Act or the Atomic Energy Act of 1954. Under regulations promulgated in May 1980, the EPA specified criteria for four properties, any one of which characterizes a waste as hazardous. These characteristics were ignitability, corrosivity, reactivity, and toxicity. Toxicity is most important to electroplating operations. EPA set up an EPA Toxicity Test. Eight of the contaminants tested for are metals, which are commonly used in electroplating. Table 4 shows the limits set for the metals tested.

TABLE 2. EFFLUENT LIMITATIONS FOR EXISTING DIRECT DISCHARGERS, EXISTING INDIRECT DISCHARGERS WITH METAL FINISHING FACILITIES, AND NEW SOURCES (METALS, CYANIDE, pH)

Effluent Limitations Mg/L Except pH

	Direct Dischargers		Indirect Dischargers Metal Finishing Facilities	
	Max Daily	Month Avg	Max Daily	Month Avg
Cd				
Existing sources	0.69	0.26	0.69	0.26
New sources	0.11	0.07	0.11	0.07
Cr(T)	2.77	1.71	2.77	1.71
Cu	2.07	3.36	2.07	
Pb	0.69	0.43	0.69	0.43
Ni	3.98	2.38	3.98	2.38
Ag	0.43	0.24	0.43	0.24
Zn	2.61	1.48	2.61	1.48
CN				
Total	1.20	0.65	1.20	0.65
amenable	0.86	0.32	0.86	0.32
pH	6–9	6–9	6–9	6–9

Source 40 CFR 433

TABLE 3. PRETREATMENT STANDARDS FOR EXISTING DISCHARGERS WITH INDIRECT NONINTEGRATED FACILITIES

(Effluent Limits Mg/L)

	Daily	Four-day avg.
Plants discharging <10,000 gallons per day		
Cd	1.2	0.7
CN (amenable)	5.0	2.7
Pb	0.6	0.4
Cd	1.2	0.7
Cr(T)	7.0	4.0
Cu	4.5	2.7
Pb	0.6	0.4
Ni	4.1	2.6
Ag	1.2	0.7
Zn	4.2	2.6
Total metals	10.5	6.8
CN(T)	1.9	1.0

Source 40 CFR 413

TABLE 4. TOXIC WASTE LIMITS SET BY EPA'S EXTRACTION PROCEDURE TOXICITY TEST

Contaminant	Extract Level
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selinium	1.0
Silver	5.0

If these limits are exceeded, or if the sludge is in any of the following categories, it is considered hazardous waste:

- Wastewater treatment sludge

- Spent plating bath solutions

- Sludge from bottom of plating baths

- Spent stripping and cleaning bath solutions

Producers of hazardous waste (generators) are ultimately responsible for proper identification, storage, transportation, and disposal of the waste. Generators are responsible for notifying EPA and maintaining records of their activities, using appropriate containers and labeling, and ensuring proper disposal. Most generators must use a manifest system which tracks the waste throughout. New requirements are constantly affecting disposal. For instance, the landfilling of bulk or noncontainerized liquids is now prohibited and land disposal may be prohibited in the future.

B. WASTE REDUCTION AND NATIONAL POLICY

Waste reduction is no longer the prerogative, but is now the responsibility of industry. The Resource Conservation and Recovery Act, as amended by the US Congress in November 1984 and supported by waste minimization provisions, states, "The Congress hereby declares it to be the national policy of the United States that, whenever feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible. Waste nevertheless generated should be treated and disposed of so as to minimize the present and future threat to human health and the environment."

This statute and related regulations have lead DOD to set nonbinding reduction goals which will become more stringent. To be met by 1992, such goals have already been established within some military departments. These are summarized as follows:

1. Office of the Secretary:

Defense Environmental Leadership Project (DELP)—Seeks innovative solutions to long-term environmental problems with cost and policy implications

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and tries to improve DOD's national leadership position in environmental protection.

Defense Logistics Agency (DLA)—Provides material support (procurement, quality control, storage, distribution, maintenance). Has instituted some informal changes in material ordering to reduce wastes created by shelf-life regulations.

2. Air Force

Office of Secretary of Air Force—Studies on decision-making and costing practices that affect waste generation.

Air Force Systems Command (AFSC)—Requested $13 million from Defense Environmental Restoration Account for waste minimization in 1986. Has completed assessment of waste minimization opportunities in eight major facilities. (US Air Force, Aeronautical Systems Division, Waste Minimization at Air Force Plants, by the Earth Technology Corporation, 1986.)

Air Force Logistics Command (AFLC)—"PACER REDUCE" waste minimization plan in place since end of 1985. Overall goal of over 50 percent reduction by 1992. Has done complete waste stream inventory by process. Studying technologies in private sector for transfer to AF operations. Some R&D conducted at Tyndall AFB by AFESC.

3. Navy:

All commands—Were required to report by April 1986 on waste minimization measures taken. The objective was to raise awareness of issues and accumulate information for transfer across commands.

Naval Civil Engineering Laboratory—Is investigating private industry initiatives for transferability and Navy operations.

4. Army:

Army Materiel Command (AMC)—Has developed a hazardous waste minimization (HAZMIN) plan. All AMC installations must implement a wide range of activities including reduction goals (15-60 percent by 1992), for major waste streams (metal working, electroplating, painting, electrical maintenance, and waste treatment sludges). Also disposal of untreated wastes in landfills to be eliminated by 1992.

C. ELECTROPLATING PROCESSES

1. General

Electroplating is the electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the basis metal. Generally, the electroplating process consists of four parts: (1) the external circuit consisting of a source of direct current (dc), a means of carrying this current to the plating tank, associated instruments such as ammeters, voltmeters, and means of regulating the voltage and current at their appropriate

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values; (2) the negative electrodes or cathodes, which are the material to be plated, along with means of positioning the material in the plating solution so that contact is made with the current source; (3) the plating solution itself, called the "bath"; and (4) the positive electrodes (anodes) usually of the metal being plated, or an inert material, used to complete the circuit. The solution is contained in a tank with a liner appropriate to the solution. A detailed description of electroplating will not be given here. References 2 and 3 can be used for this information.

Electrodeposited coatings are usually applied for the following special properties: (1) appearance, (2) protection, (3) special surface properties or (4) engineering or mechanical properties. A decorative coating may be applied for appearance "eye appeal." Inexpensive zinc die castings or ordinary steels may have a thin layer of chromium applied to enhance their appearance. A corrosion resistant coating of cadmium may be applied to equipment used in a corrosive salt spray. The cadmium will act sacrificially to protect the steel electrochemically. Special surface characteristics such as improved solderability or conductivity of electrical current may be obtained by electrodeposition of copper. Rebuilding a part to dimension by electroplating with hard nickel is one of many engineering or mechanical properties possible from electroplating of metals.

2. Cadmium and Cadmium Electroplating

Cadmium is a corrosion-resistant, soft, white metal with bluish tinges, possessing considerable ductility. The corrosion-resistant properties are of interest for cadmium electroplating.

Most cadmium plating is carried out in alkaline cyanide baths prepared by dissolving cadmium oxide (CdO) in a sodium cyanide (NaCN) solution. Sodium hydroxide (NaOH) and sodium carbonate (Na$_2$CO$_2$) are formed by functions within and are part of this bath. Cadmium balls suspended in steel wire cages serve as the plating anodes. Bath compositions and plating methods vary and depend on the purpose and the material to be plated. Other considerations include plating efficiency, plating speed, deposition uniformity, and hydrogen evolutions.

Hydrogen evolution is a major concern in the aerospace industry because of hydrogen embrittlement of high-strength steels and alloys. Every precaution is necessary to eliminate hydrogen contact with the work pieces. After plating, baking is a required to drive off hydrogen. Over 90 percent of the tensile strength of a material can be lost from hydrogen embrittlement. Because cadmium plating cannot be accomplished without production of hydrogen, the process should be optimized for minimal hydrogen production.

The vapor pressure of cadmium is 1.4 mm at 400 °C. High temperature-incineration and industrial processes lead to vaporization of cadmium into the atmosphere, where it oxidizes quickly to produce cadmium oxide. Atmospheric emissions are estimated at 16 percent of total emissions for the US on approximately 1800 metric tons per year. An estimated 70 metric tons are contributed by the electroplating process. Atmospheric concentrations in the US are usually on the order of a few hundredths or thousandths of micrograms per cubic meter of air.

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The solubility of cadmium in water is low, and pH-dependent. Cadmium concentrations in surface waters are, therefore, usually lower than 1 milligram per liter. Elevated levels occur as a result of industrial and municipal discharges, but these levels dissipate rapidly due to adsorption to suspended particles on bottom sediment. Yost (1979), Reference 4, estimated that the electroplating industry accounts for 70 percent of the cadmium discharged to sewer collection systems. Over the years, these sediments are washed to the oceans where bioaccumulation occurs in plants, shellfish, mussels, etc.

According to the EPA, land-disposed cadmium wastes represent more than 80 percent of estimated total environmental releases. This cadmium is a result of hazardous sludge disposal, and about 47 percent of this is a result of electroplating. DOD disposes of an estimated 675,000 metric tons of hazardous waste per year, of which 41 percent is accredited to the Air Force. Most of this waste contains cadmium.

A recent report by the Office of Technology Assessment stated that "ultimately, because an element cannot be destroyed, all cadmium mined eventually becomes waste: during mining and extraction, during manufacturing and industrial use, or after the disposal of cadmium containing products." This is true whether emissions are to the air, waters, or the land. Many areas, usually around industrial complexes, have reported rising concentrations, causing concern throughout the country.

Because cadmium does not occur in the pure state, it is produced as a by product of zinc, copper, and lead production. This results in an inelastic market, completely dependent on demand. Zinc production is a slow-growing industry, and cannot provide for increases in cadmium production. As a result, import of cadmium has increased over the years, until approximately 67 percent is now imported. Small fluctuations in either demand or supply could cause large price increases. The United States is the largest consumer in the world, using approximately one-fourth of the total world refined production.

The National Institute for Occupational Safety and Health (NIOSH) states that sources of potential worker exposure to cadmium include ore-smelting operations, mist from cadmium-containing electroplating baths, calcination (drying) of cadmium pigments, and handling of powdered oxide in production of cadmium soaps used to stabilize plastics. Cadmium is not essential for the health of mammals. It steadily accumulates in body tissues, especially the liver and kidneys. In humans, chronic low-level cadmium ingestion in nonoccupational settings can result in adverse health effects such as Itai-Itai disease in Japan. Recent epidemiological studies provide persuasive evidence for the carcinogenicity of cadmium oxide. The possibility of chromosomal aberrations exists. In humans, acute cadmium intoxication symptoms are severe nausea, vomiting, diarrhea, muscular cramps, salivation, sensory disturbances, liver injury, and convulsions. In fatal intoxications, these symptoms are followed by shock caused by dehydration and death within 24 hours, or by acute renal failure, cardiopulmonary depression and death within 7 to 14 days. The health effects of cadmium have brought about significant regulation. Some major legislation and regulations (Source: Office of Technology Assessment, 1986), pertaining to cadmium are cited as follows:

a. Clean Water Act

This was intended to list cadmium as a hazardous air pollutant (published 16 November 1985), based in part on EPA's conclusion that Cd is a probable human carcinogen. Decision to list will rely on pollution control techniques for cadmium and further public health risk analysis.

b. Safe Drinking Water Act

National interim primary drinking water standards (NIPDWS) of .01 milligrams per liter were set December 1975 and intended to include a fourfold safety factor to reduce earliest manifestation of chronic cadmium poisoning.

c. Clean Water Act

The water quality criterion for cadmium to protect human health is identical to NIPDWS, 0.01mg/l; set 15 March 1979. Ocean dumping was banned for all but trace amounts of cadmium (proposed 11 January 1977, finalized 6 January 1978). "Reportable quantities" on cadmium acetate, cadmium bromide, cadmium chloride were set at 100 pounds in 1979. Discharge of more than the reportable quantity into navigable waters within a 24-hour period must be reported to a national response center. Cadmium and cadmium compounds were specifically designated in a list of 65 priority toxic pollutants or pollutant categories. Cadmium and cadmium compounds are regulated for specific industrial point sources.

Applicants for NPDES permits in certain primary industrial categories with processes which discharge Cd or Cd compounds must report quantitative data on Cd discharge at each outfall.

d. Resource Conservation and Recovery Act (RCRA)

Solid waste is classified as toxic hazardous waste if it passes the toxicity test. Wastewater treatment sludges from electroplating operations are designated as hazardous, in part, because of their cadmium content. Dusts/sludges from the primary production of steel in electric furnaces and secondary lead smelting are regulated as hazardous, partially because of their cadmium content. All of these designated hazardous wastes are subject to the "cradle-to-grave" manifest system that covers generators, transportation, storage, and disposal of such wastes. Groundwater cannot be contaminated beyond the facility boundary at cadmium levels in excess of 0.01 mg/L. Oil containing more than 2 ppm cadmium is restricted for burning.

e. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

This places a tax of $4.45 per ton on manufacturers, producers, and importers of cadmium. The act taxed receipt of waste containing cadmium at $2.13 per dry weight ton. Reportable quantities are 1 pound for cadmium and 100 pounds for cadmium acetate, cadmium bromide, and cadmium chloride released into the environment. Cadmium particles need not be reported if larger than 100 micrometers.

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f. Occupational Safety and Health Act

Average exposure limit of 0.1mg/m^3 of cadmium fumes and 0.2mg/m^3 of cadmium dust; maximum exposure—0.3mg/m^3 and 0.6mg/m^3, respectively.

g. Mine Safety and Health Act

Maximum air concentrations of cadmium established for different types of mining operation.

h. Federal Food, Drug, and Cosmetic Act

Same standards as NIPDWS—0.01mg/1.

i. Hazardous Materials Transportation Act

Has established rules governing transport of cadmium acetate, cadmium bromide, and cadmium chloride.

3. Cyanide

Cadmium electroplating is especially dangerous because most cadmium electroplating baths are made up of cadmium oxide (CdO) in a sodium cyanide (NaCN) solution. Sodium hydroxide (NaOH) and sodium carbonate (Na$_2$CO$_2$) are formed by internal reactions and produce an alkaline cyanide bath. Spent plating solutions, and rinsewaters containing cyanide must be treated.

A separate treatment system is necessary to treat cyanide before metals removal. Virtually all treatment of dilute cyanide waste streams is done by alkaline chlorination. The process has been in commercial use for over 25 years, and, if properly designed and maintained, will oxidize cyanides, which are amenable to chlorination, to less than 1 ppm.

Destruction of the cyanide by chlorination can be accomplished by direct addition of sodium hypochlorine (NaCCl) or by addition of chlorine gas plus sodium hydroxide (NaOH) to the waste. Sodium hydroxide reacts with the chlorine to form sodium hypochlorite. Selection between the two methods is based on economics and safety. The chemical costs for chlorine gas treatment are about half those of direct hypochlorite additions, but handling is more dangerous and equipment costs are higher.

The hypochlorite oxidizes cyanide to cyanate. This reaction is accomplished most completely and rapidly under alkaline conditions at pH 10 or higher. An oxidation period of 30-60 minutes to 1 hour is usually allowed. The wastewater should be continuously mixed during treatment to avoid producing solid cyanide precipitates, which may resist chlorination.

The resulting cyanate is much less toxic than cyanide, but regulations require that it be further oxidized to carbon dioxide and nitrogen. This can be accomplished by additional chlorination. The pH must be kept at 8.5 so that the overall reaction rate is increased, otherwise oxidation will occur slowly over several hours. Usually, excess chlorine is used to speed breakdown.

When sodium hypochlorite is used, the reaction in the first stage is:

$$NaCN + NaOCl \quad NaCNO + NaCl$$

and in the second stage:

$$2NaCNO + 3NaOCl + H_2O \quad 3NaCl + N_2 + 2NaHCO_3$$

Sodium hypochlorite consumption is usually 25 to 100 percent greater than stoichiometric requirements. The excess is consumed by oxidation of organics and raising of the valence of metals in the wastewater.

The major costs of an alkaline chlorine cyanide treatment system are equipment installation, segregation of waste, maintenance, chemical usage, and sludge disposal. Elimination of cyanide would eliminate these costs and the savings could be used for other military O&M projects.

Table 5 summarizes the basis for costs presented in Table 6. These values are for Tinker AFB and were a result of 1986 data presented at the 1987 Airline Plating and Finishing Forum by a representative of Tinker AFB. The information is based on an 80 gpm flow rate, achieved with the practice of water conservation methods.

The bottom line is that $169,600 per year can be saved at Tinker AFB by elimination of cyanides from the plating shop. If the five ALCs have similar savings, the total yearly savings will be approximately $848,000. This is a significant savings.

TABLE 5. BASIS FOR COST ESTIMATE FOR CYANIDE TREATMENT

Item	Cost of Requirement
Electric Power	$0.05/kwh
Water:	
Alkaline sump dilution	4.2 GPM
Unit cost	$0.90/1000 gal
Chlorine:	
Volume	7.35 lb Cl/lb CN
Cost	$0.21/lb
NaOH:	
Volume	1.125 lb NaOH/lb Cl
Cost (50 percent solution)	$0.22/lb NaOH
Soda Ash:	
Adjust to pH 11:	
Dilute rinse sump	51.2 lb/day
Alkaline cyanide sump	2.7 lb/day
Cost (50 percent solution)	$0.22/lb soda ash
Chlorine tanks:	
Volume	20,000 gal
Mixing requirements	2HP/3,000 gal
Sludge haul:	
Percent solids	25 percent
Cost $0.032 per wet pound	
Labor:	
Mixed skilled and unskilled	$20.00/hr
Debt retirement capital factor (10 percent, 10 years)	0.1628

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TABLE 6. COST OF OPERATION OF CYANIDE DESTRUCT SYSTEM AT TINKER AFB (1986)

Cost Item	Alkaline Chlorine
Capital:	
Gas handling	$ 0
Tanks	37,000
Chlorine feed and mix	79,000
pH adjustment	20,000
Miscellaneous	4,500
Total capital	$140,500
Operation and maintenance:	
Mixing and gas handling	$ 4,900
Chlorine	31,800
pH adjustment:	
NaOH	37,400
Soda ash	0
Labor	43,800
Sludge hauling	21,800
Dilution water	0
Equipment Replacement	7,000
Total operation and maintenance	$146,700
Annual costs:	
Debt retirement (10 percent, 10-year)	$22,900
Operation and maintenance	146,700
Total annual costs	$169,600
Unit costs:	
Cost per pound of cyanide	$8.23

Conditions for possible serious accidents exist in the electroplating shop. Cyanide is highly toxic in itself, but when it contacts an acid, it produces lethal cyanide gases. The plating shop has many strongly acidic baths, some usually near the cyanide tanks. A mistaken addition to the wrong tank could cause a serious accident. Inhalation of concentrations of hydrogen cyanide > 300 mg/L is fatal within minutes; and inhalation of concentrations of 90–135mg/L may be fatal within 30–60 minutes.

The major point sources of cyanide releases to water are discharges from publicly owned treatment works (POTWS), iron and steel industries, and organic chemicals industries. These account for 89 percent of the estimated 14,000 Kg discharged annually to surface water. The metal-finishing and organic chemical industries account for 90 percent of the influent to POTWS, so that the metals and organic chemicals industries are the dominant sources of both direct and indirect aqueous discharges.

Cyanide is toxic to certain freshwater fish at concentrations of approximately 10 mg/L, but because cyanide degrades in the aquatic environment (half-life on the order of tens of hours), the risks to aquatic life are restricted to within a few river miles of major point sources. As an acute human toxicant is due to inhibited respiratory enzymes, resulting in anoxia. However, moderate continuous doses of cyanide can be sustained without ill effects, since detoxification mechanisms are relatively rapid. No definite studies on mutagenic or tetratogenic/reproductive effects of cyanide have been reported.

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In summary, the chemicals involved in cadmium plating are extremely hazardous to humans and their environment. The plating process can cause serious problems with hydrogen embrittlement, which can result in expensive failures with loss of aircraft and lives. Expensive treatment equipment is required both for eliminating the cyanide, and then removal of the metal. The cost of cadmium is not stable and depends on demand. Environmental regulations are becoming more stringent, and could result in an eventual ban on cadmium in the US.

4. Chromium and Chromium electroplating

Elemental chromium is a blue-white, refractory metal that exists in the earth's crust in relative abundance. The production of chromium on a commercial basis started in 1816 and has continued without interruption. Chromium compounds are now valuable in many industrial areas. Various forms of chromium are used extensively in the paint and dye industries, plating industry, steel industry for stainless steel and other alloys, chrome tanning in the leather goods industries, and in production of high-melting refractory materials. In most compounds, cadmium is found in the more stable trivalent and hexavalent states.

Chromium in an electrodeposited coating has many desirable engineering properties, some of which are: pleasing blue-white color, high reflectivity, excellent tarnish resistance, good corrosion-resistance, good wear-resistance, and good scratch-resistance. Chromium is usually divided into two categories, decorative chromium plate and engineering (hard) chromium plate. The Air Force is usually interested in engineering (hard) chromium plating.

In hard chrome plating, a chromium electrodeposit is applied in thicknesses of .002 to .05 inches (usually not more than .010) to parts such as shafts, cylinders, gears, struts, sleeves, and armatures. The deposit is used for rebuilding worn surfaces and/or to obtain one or more of the following properties: hardness, low coefficient or friction, corrosion resistance, nongalling, and nonwetting.

The chromic acid solution for decorative and engineering chromium may be the same for both, and excellent results may be obtained. If, however, best coverage and nickel activation for decorative and best plating speed for engineering use are desired, different baths and operating conditions are necessary.

The conventional solution for electrodepositing chromium has two constituents: chromic trioxide flakes (CrO_2), which combine with water to form chromic acid (H_2CrO_4); and the sulfate ion (SO_4) introduced as sulfuric acid or sulfate salt. Chromic acid flakes are added in concentrations of 20 to 60 oz/gal. The critical point is that the CrO_3/SO_4 ratio be about 100/L, although ratios between 80 to 1 and 130 to 1 are used for specific engineering requirements. There are other mixed catalyst baths, but this report does not present these baths in detail.

Chromium plating differs from most other plating operations in that an insoluble anode is used, and chromium is replenished by the addition of chromic acid. Iron anodes have been used, but are not generally suitable because they add iron to the bath and allow buildup of trivalent chromium in

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solution. Platinum has had limited success, but it allows buildup of trivalent chromium. The universally used material is lead or lead alloy, especially 7 percent tin, which oxidizes the trivalent back to hexavalent chromium during electrolysis.

Because hydrogen evolution is excessive, it is a major concern in the aerospace industry. As with cadmium, critical parts must be baked to prevent hydrogen embrittlement.

Harmful effects to man or animals seldom result from chromium in ambient air or public drinking water. Reported chromium toxicity occurs mainly from occupational exposure. Trivalent compounds are not highly toxic, but excessive exposure to dust or mists of hexavalent chromium compounds produces dermatitic skin lesions, and ulceration and perforation of the nasal septum, as well as liver and kidney damage. Incidence of lung cancer increases with long-term exposure to hexavalent chromium compounds. None of the reports suggest these compounds are mutagenic or tetratogenic risks.

Trace levels of chromium are essential to mammalian life. Irreversible metabolic damage is possible from long-term chromium deficiencies. Americans usually have less chromium in their diets than do people of most other countries and, in fact, may have marginal intake of biologically active chromium.

Sources of atmospheric chromium include emissions from coal-fired power plants, iron and steel industries, municipal incinerators, and cooling towers. Yearly averages range from below detection limits in nonurban areas to .1 mg/m^2 in urban areas. Most of the chromium in the atmosphere is particulate and most likely in the trivalent state.

Chromium concentration in soils can range from 5 to 200 ppm. The clay fraction of soils typically has a higher proportion of chromium. Chromium concentration does not change significantly with depth. Chromium in soils is mainly insoluble in adsorbed, mineral, or precipitated form. Water-extractable chromium in soils is usually less than .01 ppm. Evidence of sampling done near cooling towers suggests that hexavalent chromium is reduced naturally to the trivalent state and is readily adsorbed or precipitated.

Some chromium can be found in both surface waters and groundwaters. Freshwater concentrations are reported to range between 0-112 ppb with an average of 9.7 ppb. Concentrations in sea water ranged from 0-.5 ppb, considerably less than in freshwater. Most city drinking waters have less than 50 ppb chromium content.

For all intents and purposes, chromium in soil is immobile and mainly trivalent, having been reduced by organic matter. Flowing water transports vast amounts of chromium to estuaries to be deposited in the sediment. (For example, 790 metric tons/yr by the Susquehanna River.) The chromium remains tied up and is not raised back to hexavalent state.

Electroplating and metal finishing account for the major releases of chromium to wastewater. The sources from electroplating are from tank overflows, rinsewater, wash-down from cleaning procedures, scrubber water, etc. All of these waters must be treated before discharge. Chromium requires

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an additional step to the normal metal precipitation process. Chromium (+6) must be reduced tc chromium (+3) state, then precipitated. This requires lowering the pH to 3.0-3.5 and bubbling sulfur dioxide or adding sodium metabisulfate to the wastewater. This process is expensive because of chemical usage and equipment requirements.

After reduction, the pH of the wastewater must be raised to 7-10 to precipitate the metals. This can be done with hydrated lime or other chemicals such as caustic soda, sodium bicarbonate, etc. Excessive amounts of chemicals are necessitated by lowering and raising the pH; excessive amounts of chemicals are necessary. A polymer is usually used to help settling. The entire process is costly, as chemicals for metal treatment at Tinker AFB cost approximately $775/day, including polymer usage.

Sludge produced by the precipitation process must be disposed of as a hazardous waste. Tinker AFB pays $137/ton to dispose of hazardous waste. Tinker IWTP produces 4 to 5 tons per day of hazardous waste. Costs of disposal increase steadily, while disposal sites available decrease yearly. Future land disposal may be banned altogether.

Chromium is a strategic metal. The US has no reserves: over 95 percent of the chromium reserves in the world are in "trouble spots" (73.9 percent, Republic of South Africa; 19.7 percent, Zimbabwe; and 2.9 percent, USSR). A recent congressional research report concluded: "The US is strategically more vulnerable to a long-term chromium embargo than to an embargo of any other natural resource, including petroleum." The vulnerability of chromium and cobalt supplies represents a potential threat to the F-100 engine in the F-15 and F-16 weapons systems.

Future access to chromium is not guaranteed. Without chromium, it would be impossible to manufacture stainless steel, yet the US imports close to 90 percent of its chromium. Reference 30 estimates that a 15-26 percent reduction in imports due to a disruption in supply for 10 years would result in an economic loss of 4.2 billion dollars. The chance of such an event occurring before the year 2000 is greater than 50 percent.

New metal coating systems such as ion vapor deposition, plasma spray, substitute materials (nickel boron), etc.,could easily reduce chromium usage. Processes such as IVD do not generate waste products as chrome plating does. Economic incentives will be required to produce change. Environmental continue to provide such incentives. These techniques could be rapidly increased in the event cf severe chromium shortage.

Techniques are available to nearly eliminate chromium discharge from the electroplating shop. Dead rinses can be used to collect chromium-containing rinsewaters and return them to the plating tank as makeup water. Scrubber waters can be reduced and routed to the plating tanks. Automated spray systems can reduce water usage and automatically return chromium plating rinses to baths. Bath purifiers are available to clean the baths and eliminate disposal of used baths. The Navy has developed a system for this purpose.

In summary, chromium is generally dangerous to health only for occupational areas where inhalation of vapors, mists, or dusts is a real possibility. Chromium plating can cause hydrogen embrittlement of high-strength steels and

alloys, leading to expensive failures of weapons systems. Special treatment, with added steps and expense is required for treatment of wastewater containing chromium, and then disposal of the hazardous sludges. Nearly all chromium used in the US is imported from areas of unstable political climate. Disruption of these imports has significant probability of occurrence over the next 13 years, especially since the USSR is still pursuing "Stalin's goal of depriving the West of mineral resources of the planet." Replacing chromium plating with other techniques will require economic incentives.

5. Stripping Processes and Strippers

As electroplating has evolved, so have the processes that support the art. Stripping, rinsing, media blasting, and others are necessary to the electroplating process. Most of these processes contribute to the amounts of hazardous wastes leaving the electroplating shop and eventually to those hauled to disposal sites.

The stripping process is a major contribution of hazardous wastes from an electroplating shop. The process involves removing a thin skin of one metal from the basis metal. Many of these solutions are also used to clean or activate a surface. Examples are forms of NaCN baths which strip nickel or silver from steel, or which are used as alkaline cleaners or activators prior to silver-rhodium plating.

Salvage of plated articles is one of the major reasons for stripping and depends on removal of all or part of the metallic coating before reprocessing. The stripping process depends on the difference in chemical activity of the metallic coating and the basis metal. For successful stripping, the coating must be active and the basis metal relatively inert. A solution can always be found that will attack the coating, but only a few solutions will attack the coating without affecting the underlying metal.

Developing a stripping solution is more art than science. The basis metal may be unaffected under one set of conditions or one instance, but pit under slightly different conditions. This is particularly true when alloy composition may change from time to time. A high-carbon or an alloy steel may be pitted by a solution that will not attack a plain low-carbon steel. By changing the condition of the electrolyte or the voltage, this pitting may be minimized or avoided.

Stripping solutions vary in life and in stripping rate. Some cyanide baths may be used indefinitely since the metals will be deposited on the anode as fast as it is stripped. On the other hand, some baths will have very short lives before impurity buildup requires regeneration or disposal. As life of the bath ends, the solution must be either disposed of as a hazardous waste or treated. If the solution is treated, the cyanide must first be destroyed and then the metals precipitated. This requires two treatment processes and the equipment necessary for both. The combined cost of equipment, chemicals, and man-hours can be significant.

SECTION III

ASSESSMENT OF THE TECHNOLOGICAL STATE OF ION VAPOR DEPOSITION OF ALUMINUM FOR ELIMINATION OF CADMIUM ELECTROPLATING

A. INTRODUCTION TO ION VAPOR DEPOSITION OF ALUMINUM

The Air Force, as with its civilian counterpart, must protect products from corrosion. The stringent demands of new technologies associated with modern aircraft and support equipment for improved product life and performance have resulted in continuous investigation of new corrosion control systems. With cadmium in disfavor, and with the strong possibility of its being banned throughout the country, other corrosion prevention systems are necessary.

Ion vapor deposition is one of several similar vacuum-metallizing processes. These processes are usually performed in an airtight chamber. The chamber is evacuated to high vacuum pressures, less than 1-millionth of an atmospheric pressure, by a series of mechanical or diffusion-type pumps. While the vacuum is held, the metal is evaporated, usually by a high voltage source. Enough heat is added to produce a vapor pressure in the boiling metal considerably higher than the total pressure in the chamber. Metals leave the heated source and, in conventional systems, travel towards the outer walls of the vacuum chamber. The molecules will travel in a straight path because of the low density of air within the chamber. These systems plate line-of-sight surfaces, which means that only those surfaces that come within line-of-sight of the source during the evaporation can become coated.

The ion vapor deposition is similar in that the material is evaporated within the vacuum chamber and allowed to condense on the parts being coated. However, other features set it apart. Glow discharge cleaning and plating on all sides (now line-of-sight) are just some of the characteristics discussed later.

In the late 1960s, the search for improved corrosion protection led to government-sponsored, in-service testing of different coatings on operational military aircraft (Reference 2). These tests showed that only aluminum coating provided superior corrosion protection. Being the least dissimilar to aluminum alloy structure, it is ideally compatible. Furthermore, aluminum is anodic to steel and provides galvanic protection, as does cadmium.

Because ion vapor deposition offered particularly good potential for large-scale production applications of aluminum, it was selected for further development and evaluation. Other available processes for applying aluminum coatings such as metal spraying, electroplating, cladding, hot dipping, etc., have severe limitations. These include thickness control, adhesion, size, and shape of product that could be coated, and effectiveness on substrate properties.

The performance advantages of ion vapor-deposited aluminum were confirmed over the next several years, and the ultimate value of this process for aircraft applications was demonstrated when a full-scale production coating system was fabricated and delivered to the US Navy in 1974. Since that time,

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a military specification has been issued and coating equipment has been fabricated for the Air Force. The process is now scheduled for use on several production aerospace programs, with over 55 units in operation. Many specifications exist for ion vapor deposition of aluminum. Table 7 lists these specifications.

B. DESCRIPTION OF EQUIPMENT AND PROCESS

Two general types of equipment were developed by McDonnell Douglas for applying ion vapor-deposited aluminum, as illustrated in Figure 1. The basic components for either type consist of a steel vacuum chamber, pumping system, evaporation source, high-voltage power supply, and internal racking system. For one type, called a rack coater, this racking system is tailored for plating detail parts (normally hand-racked in electroplating). The other type, a barrel coater, has a racking system consisting of counter- rotating barrels for coating large numbers of small parts like fasteners. Vacuum locks allow for continuous mode operation.

The ion vapor deposition process has some features similar to the familiar vacuum-metallizing process, in that aluminum material is evaporated within the vacuum chamber and allowed to condense on the parts being coated. However, other features set it apart.

After the vacuum chamber has been pumped down to approximately 10^{-4} torr, it is backfilled with an inert gas to about 10 microns. At about the same time, a high negative potential is applied between the part being coated and the evaporation source. This potential ionizes the gas, and the positively charged particles bombard the surface of the negatively charged part. This intense bombardment, called glow discharge, cleans the surface and induces excellent adhesion.

Following the glow discharge cleaning, commercially available aluminum wire (1100 series) is continuously fed into resistant-heated crucibles and evaporated. A portion of the aluminum is ionized and is attracted to the negatively charged part. This results in a thick, dense, adherent coating of aluminum. The process allows the uniform coating of complex shapes because of the increased throwing power without line-of-sight limitations.

The coating sequence is the same for either type of coater. Parts are first cleaned with conventional procedures. Then the coating cycle is as follows:

1. Load parts

2. Pump down

3. Add argon

4. Glow discharge clean

5. Coat parts

6. Cool crucibles

7. Backfill and remove parts

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TABLE 7. IVD ALUMINUM COATING ACCEPTANCE

MILITARY SPECIFICATIONS

- MIL-STD-1516 – Coatings for Aircraft and Missiles
- MIL-S-5002 – Surface Treatments for Metallic Coatings for Metallic Surfaces of Weapons System
- MIL-C-83488 – Coating, Aluminum, Ion Vapor Deposited
- MIL-STD-1515 – Fastener Systems for Aerospace Applications
- MIL-S-24149B – Studs, Arc Welding and Arc Shields (Ferrules); General Specifications for Aeronautical Design Standard 13

INDUSTRY-WIDE SPECIFICATIONS

- ASTM – Aluminum Coatings
- AMS 2427 – Aluminum Plating – Ion Vapor Deposition
- AS 1650 – Procurement Specification, Coupling, Fuel, Rigid, Threaded Type

PARTIAL LISTING OF COMPANIES USING IVD ALUMINUM COATING*

- Airbus Consortium
- Bell
- Bendix
- Boeing
- Caterpillar Tractor
- Cleveland Pneumatic

- FMC
- Ford Aerospace
- General Dynamics
- General Electric
- Grumman
- Goodyear Aerospace

- Hercules
- Hughes Aircraft
- Kaman Aerospace
- Kamatics
- Lockheed

- McDonnell Douglas
- McDonnell Douglas
- Helicopter Co.
- Northrop
- Pratt & Whitney

- Rockwell
- Stanley Aviation
- Sundstrand
- Talley
- Texas Instruments

AIRCRAFT		MISSILES	HELICOPTER	PROJECTILES		MISC.
F-4	737	Harpoon	CH-2F	Copperhead	(Army)	MARK 34 Launcher
F-15	757	Peacekeeper	Apache	5" SAL GP	(Navy)	Space Shuttle
F-18	767	Patriot		SMAW	(Army)	Trident Submarine
AV-8B	SAAB 340	AMRAAM				Parachute Opening Assembly
DC-9	A-300	VL-ASROC				Supersonic Low-Altitude Target
DC-10	A-310					Latern
MD-80						
Falcon 20						
De Haviland Dush 7						
De Haviland Dush 8						

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*Most major contractors use IVD aluminum. Information on contractors using job-shops is not readily available.

Standard size chambers with associated work areas for the coating systems are shown in Table 8. Coater sizes can, of course, be tailored for specific needs.

TABLE 8. STANDARD SIZE CHAMBERS AND ESTIMATED FLOOR SPACE REQUIREMENT

Coater Type	Chamber Type	Floor Space Required
Barrel Coater	4 ft dia. x 6 ft long	20 ft x 30 ft
Rack Coater	4 ft dia. x 8 ft long	20 ft x 36 ft
	or	
	6 ft dia. x 10 ft long	24 ft x 40 ft

A typical cycle takes about 90 minutes. In the case of the barrel coater, the parts can be loaded and unloaded through the vacuum locks which eliminate the time required to pump down for each load of parts. The cycle time is then reduced to about 40 minutes.

The plating capacity of the standard size barrel coater is approximately 120 pounds (50 kilograms) of fasteners per hour. Capacity for a rack coater depends upon the size and shape of the parts. A rack coater with a translating evaporation source can coat all the parts that can be practically racked to a 5-foot wide by 10-foot long parts handling rack. A carriage rack which rotates or translates over a fixed evaporation source is also available. The uniformity of the aluminum coating achievable is comparable to that of electroplating. Note, however, that there is no significant buildup on the crests or thinning out in the roots of fasteners, which would be normally associated with electroplating.

C. COATING PERFORMANCE

Ion vapor-deposited aluminum is a soft, ductile coating of pure aluminum. On aircraft, three classes of coatings are used to obtain different qualities of corrosion protection (see Table 9).

TABLE 9. MINIMUM CORROSION PROTECTION—TYPE II

Class	Coating Thickness (Min)	Corrosion Resistance in 5% Neutral Salt Spray (HR)
1	.0010 IN	672
2	.0005 IN	504
3	.0003 IN	336

Type II has a supplementary chromate treatment and is generally used because the chromate provides additional corrosion protection necessary for satisfactory paint adhesion. Class 1 is used for most applications. Class 2 and Class 3 coatings are generally used on close tolerance parts.

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Numerous corrosion tests have been performed on ion vapor-deposited aluminum coatings at McDonnell Douglas, as well as other companies. The Air Force and Navy have both evaluated aluminum-coated fasteners in laboratory tests and on aircraft in service. As is normal with corrosion testing, tests are on aircraft in service, and results vary. The performance advantages, however, are clearly indicated.

In-service tests on fasteners, aluminum coatings outperformed cadmium (Reference 6). Similar results were obtained in laboratory tests when fasteners were exposed to SO_2 salt spray for 168 hours. Although all the fastener heads were corroded, corrosion was more severe in the cadmium-plated fasteners. More important, however, was the condition of the countersinks in the 7075 aluminum panels. The ion vapor-deposited aluminum coating provided far more protection to the countersinks.

Corrosion testing of steel panels in 5 percent neutral salt spray, per ASTM B-117, will generally show that the same thickness of bright electro-plated cadmium coating performs better than aluminum. However, the same thickness of aluminum will perform better in acidic SO_2 salt spray and in most outdoor exposure tests. Additionally, IVD aluminum can be applied substantially thicker than electroplated cadmium for applications where tolerances allow.

In aluminum panels, aluminum-coated fasteners will provide superior protection to the countersinks. In a test on 7075-T6 aluminum panels, after 2500 hours of exposure, the aluminum panel showed much more severe corrosion in the countersinks where cadmium-coated fasteners were installed.

There are also advantages for ion vapor-deposited aluminum coatings on titanium fasteners installed in aluminum structures. A comparison was made between aluminum-coated titanium fasteners installed dry and bare titanium fasteners installed with wet epoxy primer (a standard procedure on aircraft). The fasteners were installed in 7075-T6 aluminum alloy that had been treated with MIL-C-5541. The panel was sprayed with one coat of MIL-C-2377 primer and exposed to SO_2 salt spray for 28 days. Visual examination showed that the blistering of primer around the peripheries of the bare fasteners was more severe than around the aluminum-coated fasteners. The countersinks also showed less corrosion where the aluminum-coated fasteners were installed.

Studies at McDonnell have also shown a cost advantage of using ion vapor-deposited aluminum-coated fasteners in lieu of wet installation.

A large amount of fastener qualification data has been generated on the use of ion vapor-deposited aluminum. A small portion of the data is presented here. Two conclusions are: (a) ion vapor deposition of aluminum is not detrimental to the substrate mechanical properties, and (b) the coefficient of friction of aluminum is higher than cadmium, therefore, higher installation forces are required. However, in most cases these higher values are within the working ranges presently used for cadmium. (The use of interference fit fasteners may require closer attention to lubricants.)

Although the ion vapor deposition process would not be expected to cause hydrogen embrittlement, stress durability tests were performed in accordance

with MIL-STD-1312, Test 5. Aluminum coated H-11 alloy steel bolts were stressed to 90 percent of the minimum ultimate strength. The tests were discontinued after 11 days without failure (Reference 3).

Higher usable temperature of 925°F to cadmium's 450°F allows stress rupture tests at 800°F to be performed on H-11 steel aluminum-coated bolts. A load equivalent to 75 percent of the bolt ultimate tensile strength was applied for 200 hours. No failures occurred (Reference 7).

Tension fatigue tests were also made on fasteners, following the procedures specified in Test 11, MIL-STD-1312. The tests were conducted with R = +0.1. The data showed ion vapor-deposited aluminum to be slightly better than cadmium.

As stated, the coefficient of friction for the ion vapor-deposited aluminum is slightly higher than for electroplated cadmium. The difference, however, is generally not significant enough to require a change in installation procedures.

In torque-tension relationships, even without dedicated development work to optimize nut materials, lubricants, and crimps for ion vapor-deposited aluminum-coated bolts, galling and seizing are either insignificant or manageable. This was also confirmed in reusability tests.

D. PRODUCTION APPLICATIONS

Both rack-and-barrel type coaters have been produced and are operating in production environments. Primary applications of ion vapor-deposited aluminum in aircraft include the replacement of electroplated cadmium, diffused-nickel cadmium, vacuum-deposited cadmium, sacrificial paint-type coatings, and anodized coatings. In addition, aluminum can be applied to parts previously left unplated because of inadequacies in the other available coatings.

A large rack coater 7 feet (2 meters) in diameter by 12 feet (3.7 meters) long, was put into operation at McDonnell Aircraft Company, St Louis, in 1976. Steel parts for the F-4 Phantom and F-15 Eagle aircraft, plus some engine components, were coated in that equipment. As a result of the new process, some stainless steel parts have been changed to aluminum-plated alloy steel at a cost savings. This is possible by taking advantage of the aluminum coating's compatibility with fuel and titanium and its higher temperature capability.

The aluminum wing skins, placed in the chamber together, have the largest plan area coated to date. Sulfuric acid anodizer was formerly used on these fatigue-critical parts. While the brittle anodic film reduced fatigue strength, the aluminum coating resulted in no fatigue strength reduction. No design change was necessary. The substitution also eliminated a shot-peening operation, resulting in cost savings.

Ion vapor-deposited aluminum is also used on the Harrier aircraft, and is the primary corrosion-protective plating on the F-18 Hornet. On the Hornet, it is used on all fatigue-critical aluminum structures, on alloy steel structure of all strength levels, on titanium and steel fasteners, and for electrical bonding and EMIC applications.

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Two slightly smaller (standard size) rack-type coaters are available. The coater delivered to the Navy in 1974 is 4 feet (1.2 meters) by 8 feet (2.4 meters), and the Air Force coater is 6 feet (1.8 meters) by 10 feet (3 meters). A typical application for these coaters might be the replacement of cadmium on aircraft landing gears or jet engine components. In addition, the rack-coater, with tailored internal racking systems, is being procured by commercial companies with their own plating facilities and by job shop platers.

In addition to the use of ion vapor-deposited aluminum on aircraft and engine hardware limited to 925°F, there is a growing interest in potential application in the high-temperature turbine section of jet engines. After deposition in the standard way, the aluminum coating is diffused into the base metal to produce the constituents of a good, high-temperature turbine blade coating. Compared to pack cementation, preliminary tests of the diffused aluminum coating have been very encouraging.

The IVD aluminum coating has been used recently as a substitute for anodizing on fittings requiring electrical continuity. For aluminum alloy fuel and pneumatic line fittings, IVD aluminum provides an electrical bond across the fitting which dissipates static electrical charges generated by fuel or airflow. At the same time, it protects the fitting against corrosion. With anodizing, a bonding jumper or other technique is needed to establish the required conductive path. Substantial cost savings are realized by eliminating the bonding-jumper installation step. IVD can replace anodize, aloeline, and most other conversion coatings on aluminum alloys.

IVD aluminum is also being used in place of electroplated tin for electrical bonding and electromagnetic interference compatibility (EMIC). The IVD coating offers protection superior to electroplated tin against corrosion of aluminum alloys. The aluminum coating is sacrificial to the substrate, whereas tin is not. As a result, the IVD aluminum has replaced the commonly used electroplated tin for many aircraft applications where aluminum structure-to-structure interfaces must meet EMIC requirements. When treated with a chromatic conversion coating per MIL-C-5541, and when normal joint clamp-up forces are used, the IVD aluminum will provide lower joint resistance after exposure to corrosive environments than will the tin electroplate (Table 10).

The use of IVD aluminum, instead of the tin, is cost-effective not only because of higher performance and less maintenance, but also because processing steps such as masking, and processing problems such as poor adhesion of the electroplated tin, are eliminated.

TABLE 10. RESISTANCE MEASUREMENTS OF EMIC ASSEMBLIES*

Interface Coating	Resistance Before Exposure (milliohms)	Resistance After Exposure (milliohms)
Electroplated tin	0.03 – 0.05	200,000
IVD Aluminum	0.25 – 1.3	0.32

*Testing consisted of 1-year exposure on the flight deck of an aircraft
carrier in service.

E. PROMISING APPLICATIONS

Two promising ideas exist for future applications of IVD aluminum. The
first is as a substitute for cadmium plate and anodized coatings on electrical
connectors. IVD aluminum can replace both the cadmium plating and the copper
or nickel plating normally required for electrical connectors. IVD aluminum
provides the needed electrical conductivity, along with corrosion protection,
that doubles the 500-hour salt-fog requirement of MIL-C-38999. Connector
details that are not required to be electrically conductive are normally
machined from wrought-aluminum alloy stock and anodized. IVD aluminum can be
applied directly to a casting, and where required, the coated part can be
anodized. A casting coated with IVD aluminum and anodized is usually far less
expensive than an anodized, wrought detail.

The second promising application centers on IVD as a substitute for
flame- and arc-sprayed coatings to provide EMI shielding and nuclear hardening
of nonmetallics. Efforts are underway to evaluate the cost-effective
manufacture of electronic enclosures using injection-molded thermoplastic
materials. These enclosures often require EMI shielding, and if military
applications also require nuclear hardening, IVD aluminum is a promising
candidate. With only minor variations in the normal processing parameters for
metallic parts, a dense, adherent coating of aluminum can be built up on
thermoplastic materials by ion vapor deposition until a thickness of 5 mils or
more is achieved. The IVD aluminum with a chromate conversion coating provides
the necessary EMI shielding, nuclear hardening, and grounding requirements.
Also, preliminary testing has shown it to be more uniform and less porous than
flame-sprayed coatings, and more durable than organic coatings.

F. ECONOMICS

Over recent years improved reliability and increased productivity have
resulted in a cost-competitive process. Typical costs shown in Table 11 are
based strictly on material, energy, and manpower costs, ignoring environmental
savings.

In a recent study conducted by Kelly AFB TX (1985), manpower savings
estimate a 75 percent reduction in labor over typical cadmium electro-
plating. Ni-Cd has a minimum of 12 steps and can have 24 or more steps,
depending on materials, condition, and configuration restraints requiring many
man-hours. In this study using AFLCK-78-3 guidance, $74,753 was saved
annually. This results in a present value benefit of $459,325, with

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TABLE 11. ECONOMIC EXAMPLES FOR IVD OF ALUMINUM

IVD Type	Coater Capacity	Cycle	Throughout	Material and Energy Costs	Labor Requirement[1]
Std. Rack	50 Ft^2 Work Area	1.50 hr	33 Ft^2/hr2 (Ft. note 2)	$20/hr	1.8 Man-hours
Std. Barrel	120 lb Steel Fasteners	.75 hr	160 lb/hr	$25/hr	2.0 Man-hours
Derivative Barrel	600 lb Steel Fasteners	1.25 hr	480 lb/hr	$40/hr	2.5 Man-hours

[1]Includes part preclean, part processing and part posttreatment.
[2]The maximum flat plate area that can be coated per cycle is 50 square feet. The total surface area of parts that can be coated depends on part configuration and the number of parts packed in 50 square foot areas.

a saving/investment ratio of 1.36. These values, of course, would increase with increased production or more shifts. As per AFLCK-78-3, this study was based on an economic life of 10 years, but actual practice at Long Beach Naval Shipyard indicates this equipment may last up to 13 years. Other cost benefits not included here would increase the economical benefits. Environmental aspects is one area discussed separately. The point is, this process stands on its own and is cost-competitive without environmental benefits added.

G. ENVIRONMENTAL HEALTH AND SAFETY CONSIDERATIONS

Cadmium is very toxic, with many harmful side effects (Section 1), and even small concentrations can damage the environment. Cadmium is so toxic that Sweden has banned its use or the import of products containing cadmium. California may follow the example, and the country usually follows California on environmental issues. This will leave the ALCs, such as McClellan AFB in California, with the necessity of either replacing cadmium or facing legal repercussions.

Cadmium plating solutions are usually cyanide-based. Cyanide is useful because it complexes with so many metals and the complexes vary greatly in their strength or formation constants. This shift to more negative values crowds the electrode potentials closer together.

While cyanide is greatly beneficial to the plating process, it is highly toxic, dangerous to work around, and is harmful to the environment (Section I). When cyanide comes into contact with an acid, it produces lethal cyanide gases. Because each Air Force plating shop contains large quantities of both cyanide solutions and acids, each shop is a potential "Bhopal disaster," where a release of a cyanate gas killed thousands.

Treatment of cadmium plating solutions and rinsewaters is expensive. It is usually a two-step process requiring the destruction of cyanide, followed by precipitation of the cadmium. Both steps require separate tanks, instrumentation, chemicals, and man-hours. Initial investment on treatment

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systems can run into several hundred thousand dollars with no payback, except to remain in compliance with regulations. These overhead costs run up the cost of production for each item plated.

After precipitation of the cadmium, the hazardous sludges formed must be disposed of in a hazardous waste disposal site. This costs each ALC hundreds of thousands of dollars each year, with costs constantly rising. Even if EPA bans land disposal of hazardous wastes, "Cradle to Grave" legislation says the Air Force is still responsible for that material. Another defense environmental restoration program may, with billions of dollars, clean up the cadmium wastes disposed of this year.

Cadmium plating usually requires lined, stainless-steel tanks, or equivalent, which can hold 1500 gallons or more. Each tank is filled with a solution which must be maintained by a chemist, and disposed of when contaminated. Estimates run as high as $12,000 per tank, per year to service them. Ventilation must be installed around each tank which, connects to a scrubber system. Each scrubber system runs hundreds of thousands of dollars to purchase and maintain.

Cadmium is a soft metal and, as such, easily contaminates stripping solutions removing paint from an aircraft, or blast media stripping paint from an aircraft. Over 1500 pounds of blast media is disposed of from a stripping operation and is considered hazardous waste. Over 200 aircraft stripped by plastic beads at Hill each year generate 300,000 pounds of beads to be disposed of as hazardous waste. At a $.20-per-pound disposal fee, this results in $60,000 each year for this one item. The two things that make the beads hazardous materials are chromium from the paint and cadmium from the cadmium-plated rivets. Nonchromium primers and paints are being developed now and will be used in the future. Elimination of cadmium (which can be done) would result in nonhazardous blasting that could be disposed of for only several dollars a ton.

Cadmium is a byproduct of zinc production, which is slowly growing; therefore, the supply of cadmium is not very elastic. Roughly 50 percent of total consumption is for electroplating. A new use of cadmium (accounting for 20 percent) is as a stabilizer for polyvinyl chloride. Pigments account for another 20 percent, and 10 percent is attributed to miscellaneous use.

The use of IVD of aluminum to replace cadmium electroplating would eliminate all environmental problems associated with the process without introducing new ones. Health and safety problems would be eliminated because aluminum is not a hazardous material and the process does not require cyanide bases, tanks, special ventilation, or rinsewater. It produces no hazardous sludges and requires no waste treatment facilities. All unused aluminum is recoverable, and a superior product is produced.

H. RECOMMENDED RESEARCH PROGRAM

Since its conception in the 1960s, IVD has become a viable, competing production process. Based on the lists of Cadmium and Ni-Cd plated parts supplied by the ALCs, and previous studies completed on components over the last decade, approximately 85 percent of components now plated with cadmium can immediately be changed to IVD of aluminum. The other percentage is

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composed of inside diameters, and erosion control surfaces. Testing and possible new surface coatings may be necessary to eliminate that 15 percent.

The recommended research program would be in two phases. Phase I would be a paper study with the following objectives: (1) Compile a "complete" list of all cadmium-plated parts at the ALCs, collect all data on previous testing of IVD, contact aircraft and engine manufactures and appropriate ALC personnel to determine testing required to technically justify technical order change, and try to develop a generic testing program. (2) Provide technical justifications for all parts similar to those already tested. (3) Provide cost justifications which include processing and environmental, health, safety, and life-cycle costs. (4) Update military specifications to provide for IVD of aluminum on parts which have been technically justified.

Phase II would be to provide a demonstration site for elimination of cadmium. Phase II would have the following objectives: (1) Test those parts which cannot be technically justified on experience. (2) Develop methods or coatings to eliminate cadmium on those parts necessary. (3) Modify military specifications to eliminate cadmium plating of these parts. (4) Provide necessary equipment and expertise for a demonstration to eliminate cadmium plating at an ALC. Phase II would be to follow the same procedures outlined in Phase I, Task 2, for all ALCs.

I. COST ESTIMATE

Year 1   Data collection, testing development, technical evaluation of cadmium-plated parts for immediate conversion to IVD of aluminum, process specification alternatives development, some testing of parts (Air Force-wide). This would cost an estimated $400,000.

Year 2   Selection of demonstration site for complete conversion to IVD of aluminum, continued testing, initiation of demonstration site, at an estimated cost of $850,000.

Year 3   Testing of remaining parts throughout the ALCs and modification of process specifications, provide operations and maintenance manuals, and health and safety requirements.

Cost estimate would be $500,000.

J. SUMMARY

Even small amounts of cadmium can be harmful to both health and environment. Cadmium plating solutions are usually cyanide-based. Cyanide is also hazardous and, when mixed with acid, releases gases similar to the cyanate gas that killed thousands in the Bhopal disaster.

IVD of aluminum can feasibly eliminate cadmium plating. This would eliminate disposal problems and associated costs, help prevent future "superfunds" sites, eliminate health and environmental dangers, and avoid waste management liabilities.[1]

IVD of aluminum provides a proven, superior coating for prevention of corrosion. Numerous studies, a military standard, and a military specification recommend the process, which is both nontoxic and cost-competitive. Over 85 percent of cadmium plating can be eliminated initially, and the remaining 15 percent can be eliminated through testing and process modification.

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[1]Waste management, as defined by the Office of Technology Assessment, is "All nonproductive hazardous outputs from industrial operations into the environmental media, even though they may be within permitted or licensed limits."

SECTION IV

TECHNICAL ASSESSMENT OF NONCYANIDE REPLACEMENTS
FOR CYANIDE STRIPPING BATHS

A. INTRODUCTION TO THE STRIPPING PROCESS

Development of a stripping solution is as much an art as a science. The same principles apply to noncyanide stripping solutions. Most noncyanide strippers on the market are proprietary. Those that are not proprietary are simple, widely used chemical combinations that have been used for decades.

Cyanides are dangerous to health and environment (Section I). Cyanide strippers contribute to the cyanide wastes which reach the IWTP by way of wastewater. They must be treated, usually by alkaline chlorination. These strippers have been used to remove various plated metals from substrate metals, and are usually contaminated with these metals. These solutions and the wastewater resulting from them, are difficult to treat because of the presence of stable ferrocyanides, and other cyanide complexes not amenable to chlorination. Since many discharge limits are based on total cyanides, some facilities having cyanide strippers may find it difficult to avoid permit violations.

Regulatory and economic pressures resulting from environmental considerations have resulted in development of many noncyanide stripping baths. Choice baths are usually left to individual commands. This has resulted in DOD electroplating shops with a variety of stripping processes which have been tested and found satisfactory, but which are not necessarily used DOD-wide. Better communication between DOD components could eliminate most cyanide stripping baths. Enhanced communication with the private sector would also result in other proven processes to transfer.

B. STATUS OF THE ALCs STRIPPING PROCESSES

Recently, information was requested about the cyanide and noncyanide strippers at each of the ALCs. Environmental and Industrial Management (MAQCD) at McClellan AFB was the lead center for gathering the information. Table 12 lists cyanide strippers in use, while Table 13 lists noncyanide strippers in use today as reported by MAQCD.

TABLE 12. CYANIDE STRIPPERS IN USE AT ALCs

ALC	Cyanide Stripper	Application
McClellan AFB	NaCN (8-12 OM/gal) NaOH (8-12 OM/gal)	Strip silver from steel
McClellan AFB	NaCN (8-12 OM/gal) NaOH (8-12 OM/gal)	Activate DEAC steel prior to silver-rhodium plating
McClellan AFB	NaCN (7-16 OM/gal)	Treat steel alloys prior to cadmium plating
Tinker AFB	NaCN (10-14 CM/gal) NaOH (1-3 OM/gal)	Strip silver
	NaCN (10-14 OM/gal) NaOH (2 OM/gal) m-nitrobenzene Sulfonate (8 OM/gal)	Strip nickel
	NaCN (8-14 OM/gal) NaOH (18-24 OM/gal)	Alkaline cleaner
Kelly AFB	NaCN (12 OM/gal) NaOH (2 OM/gal)	Strip silver
	NaCN (12 OM/gal) NaOH (2 OM/gal) m-nitrobenzene Sulfonate (8 OM/gal)	Strip nickel
	NaCN (12 OM/gal) NaOH (8 OM/gal) m-nitrobenzene Sulfonate (8 OM/gal) Enthone, Inc, Enstrip TL (16 OM/gal)	Strip tungsten Carbide
Hill AFB	NaCN, NaOH NaCN, NaOH m-nitrobenzene Sulfonate	Strip silver from steel Strip nickel from steel
Robins AFB	NaCN, NaOH NaCN and MacDermid Inc, metex strip aid	Strip silver from steel Strip cadmium and nickel from steel

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TABLE 13. NONCYANIDE STRIPPERS IN USE AT ALCSs

ALC	Noncyanide Strippers	Application
McClellan AFB	Shipley Company, Inc, electroless nickel stripper 424D and 424L	Strip electroless nickel from steel
	Ammonium nitrate	Strip cadmium from steel
	Chromic acid	Strip chrome from aluminum
	Sodium hydroxide	Strip chrome from steel
	Hot sulfuric nitric acid	Strip precious metals from copper-based alloys
	Nitric acid	Strip nickel from aluminum
Tinker AFB	None	
Kelly AFB	Enthone Enstrip GT 317	Strip tungsten carbide
Hill AFB	10 percent sulfuric acid	Strip nickel from aluminum
	Sodium hydroxide	Strip chrome from steel
	Ammonium nitrate Chromic and phosphoric acid	Strip cadmium from steel Strip anodize
Robins AFB	Tetra potassium Pyrophosphate	Strip chrome from steel
	Potassium hydroxide and proprietary compounds. (M&T Chemical, Inc, Unichrome 80)	
	Proprietary acidified peroxide solution (Chemlink Division [T-Strip] and Surface Chem Corp [Lead-Off])	Strip tin-lead solder from printed circuit boards

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A review of Tables 12 and 13 indicates that tested substitute processes may be available between the ALCs. For example, at Robins AFB a cyanide stripper is used to remove cadmium from steel, while at Hill AFB, ammonium nitrate is used for the same purpose. Of course, the brief description of the application may not include some important parameters such as solder joints or brazing, etc., which may have limited selection.

C. NONCYANIDE ALTERNATIVES

The lack of communication DOD-wide, and throughout the civilian community, is improving development of alternative processes. Other DOD groups are using processing that could do the job as well for the Air Force, but those have not been adopted by the ALCs. An example of this may be the Tungsten carbide stripping process under NAVAIR specification 028-70A-6-2. These processes have been thoroughly tested and would be easy to transfer.

Many factors can cause a process to be overlooked. Some of these are: technical justification, economics, habit, communication, and time restraints. Technical justification for a change in process specification can require a great deal of time, effort, and money. Sometimes excessive amounts of testing are required, even when similar work has been completed. This may be required, even through knowledgeable personnel know the process is acceptable. These types of technical hang-ups can result in disuse of a process because of the trouble involved in obtaining the approval. Under these conditions, the problem of process change will occur quickly if severe economic or process-oriented reasons apply. One must realize that very little happens to change production processes that isn't based on strong economic advantages, or strong production incentives. Production time is lost during change, people must be trained, and new process specifications must be developed. Environmental regulations and requirements are now providing those incentives.

Habit is hard to overcome. If workers have been using a process for a number of years with good results, they become attached to that process. Anything different requires a loss of "comfort," redevelopment of old skills, or learning new skills. For many workers this is undesirable, and management may have trouble convincing personnel of the benefits derived from change.

Communication between government branches, civilian counterparts, and even internal groups of one organization can be poor. This can be attributed to proprietary information, or sensitive material or to a lack of publicity of a process. Periodic studies should be conducted within industry to determine if a common problem has an available solution.

Time restraints apply to all production work. Many employees who review processes are too busy to search for alternative processes or to provide testing for new processes when the old process seems to work well. Thus, a viable alternative may be rejected for the wrong reason, because evaluation of the process involves more time.

Table 14 is a result of a very limited search for a noncyanide process to replace those listed. These cover those requested by the ALCs. Applicable notes are given at the bottom.

TABLE 14. ALTERNATIVES TO CYANIDE STRIPPERS IN USE AT ALCs

	Application	Cyanide Process	Noncyanide Alternative
1.	Strip silver from steel[1]	NaCN (8–14 oz/gal) NaOH (1–12 oz/gal)	Potassium nitrate Ammonium hydroxide
2.	Activate DGAC steel prior to silver-rhodium plating[2]	NaCN (8–12 oz/gal) NaOH (8–12 oz/gal)	Hydrochloric acid
3.	Treat steel alloys prior to cadmium plating [3]	NaCN (8–16 oz/gal)	Hydrochloric acid
4.	Strip nickel from steel [4]	NaCN (8–12 oz/gal) NaOH (2–8 oz/gal) m-nitrobenzene sulfonate (150°F) (4–8 oz/gal)	a. Sulfuric acid, 3 gal H_2O, 2 gal Room temperature Reverse current, 6 volts Lead cathode Copper sulfate or glycerine (4 OM/gal)

a. Sulfuric acid, 3 gal
   H_2O, 2 gal
   Room temperature
   Reverse current, 6 volts
   Lead cathode
   Copper sulfate or
   glycerine (4 OM/gal)

b. Fuming nitric acid
   Room temperature

c. Nitric acid (concen-
   trated), 1 gallon
   Hydrochloric acid,
   1 fl oz
   Room temperature

d. Same as (c) with 1/2 oz
   sodium instead of
   hydrochloric acid

e. Sodium nitrate, 4–5 lb/
   gal 100 amp/fy^2 minimum
   Reverse current, 200°F
   at 6 volts
   Steel cathodes, pH 6–8,
   agitation

f. Sulfuric acid 50% by vol
   Anodic 2 volts, lead
   anodes
   50–55° baume

g. Many proprietary products
   provide good stripping

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TABLE 14. ALTERNATIVES TO CYANIDE STRIPPERS IN USE AT ALCs (Concluded)

Application	Cyanide Process	Noncyanide Alternative
5. Alkaline cleaner[5]	NaCN (8–14 oz/g NaOH (18–24 oz.	See note:
6. Strip tungsten carbide[6]	NaCN (12 oz/gal) NaOH (8 oz/gal) m-nitrobenzene Sulfonate (8 oz/gal) Enthone, Inc, Enstrip TL (16 oz/gal)	50 g/L rochelle salts 200 g/L sodium carbonate 160–180°F .6 amp/in^2
7. Strip cadmium from steel[7]	NaCN NaOH	Ammonium nitrate

NOTES:

[1]Most electroplating facilities ship the spent baths to a recovery facility; therefore, they do not perceive a problem cnanged.

[2]The silver-rhodium bath is probably a cyanide bath, and the operators feel that they can go from a cyanide strip to a cyanide plating bath without problems.

[3]Hydrogen embrittlement may be the concern with this process, but with a mandatory bake step, this should not be a problem.

[4]See included list of proprietary products that are used by DOD and industry.

[5]There are too many alkaline cleaners to mention, but there should be no reason to make it necessary to use a cyanide-based cleaner. Usually hydroxides, silicates, and carbonates are used with sequestering agents, dispersants, and various surface-active ingredients (120–200°+) (1/2–2 lb/gal).

[6]Developed by Rolls Royce, NAVAIR specification 028-70A-6-2, capable of 5 thousandths/30 min.

[7]Industrial standard process.

As stated previously, many proprietary products on the market for stripping are not cyanide-based, have been tested by DOD, and have military specifications available. A partial list of some major DOD supplies follows:

McGean-Rohco, Inc, Cleveland OH (216) 441-4900
  Rostripelectrolytic stripper SP. A powered electrolytic stripper to remove copper, nickel, and other metals from steel parts when electrolitic current is used (no cyanides or amines).

Witco Corp (Allied Kelire) Des Plaines IL 1-800-323-9784 (Mark Farver Product(s))

ARP 66. A high-speed, cyanide-free immersion stripper for electroless nickel deposits—strips all types electroless nickel without attacking substrate.

ARP 4. Liquid chelating agent.

ARP 60 Application 2. Strip from brass.

ISOPREP 177. Powdered alkaline descale

Process 235L. Liquid alkaline descale.

Process 235 CXCF. Alkaline descale additive.

Enthone Inc, New Haven CO (203) 934-8611 (Frank Brindisi Products)

ENSTRIP NP (alkaline). Strips watts-type and sulfamate nickel from steel with copper alloy and silver brazed details.

ENSTRIP N-190. Strips nickel from steel and copper without ammonia on cyanide.

ENSTRIP S-180. Stripper for nickel, nickel sulfamate, nickel iron, and copper from steel.

ENSTRIP GT-317 Strips tungsten carbide

ENSTRIP EN 79. Stripper for electroless nickel from steel and copper alloys.

ENSTRIP EN 86. Stripper for electroless nickel from steel and copper alloys.

ENSTRIP L-90. Immersion stripper for nickel, copper, and other metals from aluminum and stainless steel.

ENSTRIP GT-317. Stripper for tungsten and carbide from titanium, steel, and stainless steel.

Other companies were either not contacted or did not respond within the required time limits.

D. RECOMMENDED RESEARCH PROGRAM

Because of the abundance of commercial interest and the number of baths available, it appears unnecessary for HQ AFESC to devote research time to develop "new" stripping processes. Instead, available noncyanide processes used both by DOD and commercial facilities should be investigated and results should be provided as a data bank for use by plating facilities. Available military standards, military specifications, and user identification should be included. The noncyanide strippers noted in this report should be investigated, along with others that show promise for incorporation into ALC plating facilities.

E. COST ESTIMATE

Year 1: Develop database and change processes where technically justifiable. $300K

Year 2: Test processes where necessary. $500K

Year 3: Develop noncyanide strippers if needed. $200K

F. SUMMARY

Development of stripping solutions is advanced and many proprietary and nonproprietary noncyanide stripping solutions are available to industry. Noncyanide strippers will help eliminate cyanides from the plating shop. This will reduce treatment costs, and provide a safer industrial environment. Regulatory approaches encourage use of noncyanide strippers.

Proven tested alternatives are available to replace the cyanide strippers reported by the ALCs. Most of them have DOD specifications or standards that apply. A survey should be conducted throughout DOD and the industry to provide a database of processes and parts already tested. The database should include existing standards, specifications, etc. Wherever necessary, a generic testing program should be conducted for technical justification. Qualified Products Lists or performance-related specifications should be developed wherever applicable.

SECTION V

PLASMA SPRAY AS A REPLACEMENT FOR CHROMIUM ELECTROPLATING

A. INTRODUCTION TO PLASMA SPRAY

Thermal spraying is a method of melting and transporting materials at high velocities to coat other surfaces. Techniques vary from oxyacetylene torches to plasma generators, some of which may be operated in a vacuum. Coatings available are dense, adherent, and temperature-resistant, with high integrity. As a gas, plasma has enough energy content to ionize a significant portion and will then conduct electricity. Plasmas are sustained by continued passage of electrical current through the gas. For the high-temperature plasmas, local thermodynamic equilibrium is obtained with electrons and ions at the same energy level.

Typical plasma spray techniques pass a suitable gas through a high-current arc, creating the plasma. Thermal balance is charged by constricting the arc, which can raise the temperature to as high as $40,000^\circ C$. The typical system has the plasma arc spray gun, a power feed, a plasma arc control unit, a gas control unit, power, water, and gas supplies.

B. DESCRIPTION OF EQUIPMENT

The most important piece of equipment is the plasma torch, a highly engineered piece of equipment. In the torch, a gas, normally argon or nitrogen, flows around a tungsten cathode and between it and a copper anode. With the gas flowing, a high-frequency electrical discharge is used to initiate a direct current arc between electrodes, carried by the ionized gas plasma. A region of extremely high temperature is produced, into which powdered materials are injected and propelled towards a target. Power consumption is usually 5-80 kilowatt with temperatures ranging from $10,000^\circ C - 40,000^\circ C$. Cooling water is used to control temperatures where needed to preserve equipment.

Plasma temperatures and gas velocities are governed by electrode geometry, gas density, current-voltage conditions, and mass flow rate. Arc core temperature depends on the extent to which the arc is restricted inside the torch. This restriction is achieved by reducing the anode bore diameter and by utilizing thermal and magneto hydrodynamic pinch.

High temperatures cause gas expansion, which provides energy for spraying. Velocities controlled by geometry can achieve supersonic flow rates. Powder velocity depends on mass flow rate and distance of travel. Velocity ranges are reported between 120-550 meters second.

Powder injection should be uniform and introduced in such a way as to allow long resident times. Problems have been reported with powder adhesive adhering to the throat of anodes and resulting in blockage and overheating. Consequently, most manufacturers inject powder either where the nozzle diverges or just beyond the exit. Ideally, the powder should be injected upstream of the anode for a more complete melt. Research is continuing with powder injection systems. Other components such as gas, water, and electrical power equipment are typical to other industrial processes.

C. STATE OF THE ART

Plasma spray techniques are used to apply a multitude of materials, including the following:

- Metals

- Metal Alloys

- Ceramics

- Cermets

- Plastics

- Composites

- Refractories

- Mixtures of all the above

The list of materials being applied is almost infinite and constantly growing. Uses include application of bonding materials, abrasives, abradable clearance control coatings, salvage or repair materials, wear protection materials, instrumentation base materials, corrosion protection materials, heat-resistant materials, and many special-purpose deposits. Some specific materials include nickel aluminum, molybdenum, silicon aluminum, cermet, aluminum titania, nickel chromium, and other nickel chromium alloys, carbon and stainless steels, carbides, and many more. Thicknesses range from less than 0.001 inches to 0.1 inch, or greater; usually, 0.003 inches to 0.015 inches. Coatings can be dense, adherent with possible porosities of less than 1 percent with conventional equipment.

Some problems reported with plasma spray techniques are high-oxide deposits, poor adhesion, low densities, and high residual stresses, all of which result in negative mechanical reliability of the coating and reduction of oxidation/corrosion protection properties. Some available techniques can eliminate these problems.

New plasma spray guns allow operation at up to 80 kilowatts of power with a single gas, argon. The new technology incorporates arc stabilization, coupled with closed-loop voltage control, resulting in the ability to tailor the plasma plume through control of plasma gas flow, arc voltage, and arc current. The guns are built to use only argon, which reduces the possibility of embrittlement caused by hydrogen or nitrogen. Arc stabilization produces a fuller plasma plume, improving the temperature profile at the nozzle which results in improved melt characteristics and thus, improved adhesion. Research and development in this area is continuous in the civilian sector.

Extensive work is going on in developing new powders for plasma spray techniques. The powders must be chemically pure and homogeneous, with uniform size and low-gas content. Many new materials are available to use for just about any purpose. These materials are constantly being evaluated

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for performance characteristics useful to the aerospace industries. Many of the coatings developed for a specialized function can often provide more reliable mechanical functioning.

A process that has opened up many ways of improving deposit characteristics is vacuum plasma deposition (VPD). Completely controlling the spray environment in a vacuum of less than 100 torr, it permits higher gun and substrate temperatures, eliminates substrate oxidation, and leads to improved deposit efficiencies. Substrates can be preheated to 760-1038°C, greatly enhancing adhesion. Preliminary roughing can be eliminated with the plasma gun used to sputter clean and slightly erode the part. Since deposition is accomplished at high temperature, the particles are immediately recrystallized after solidification, eliminating residual stresses which allow thicker coatings. Deposits are recrystallized and annealed in situ, resulting in stress relief. Effluent velocities are much higher in a vacuum, resulting in a greater density coating.

Laser processing is a new developing process used in conjunction with plasma spray techniques. This technique modifies an applied coating by remelting the applied coating and a minor portion of substrate surface by scanning the coating relative to the focused laser beam to produce melting. Resolidification results in reduction or elimination of structural inhomogeneities. Coating adhesion and general mechanical properties are significantly improved by alloying with the substrates and development of a metallurgical bond. The process greatly reduces porosity and subsequently reduces potential.

Automated systems for plasma spray techniques are being developed. A computer-controlled industrial robot can provide consistency and flexibility, resulting in high quality, reproducible coatings for complicated parts. Robotic manipulation can do repetitive, relatively dangerous work with no adverse effects. Rigid control of parameters and environment results in superior coatings. Robotic configurations would allow many parts to be completed before breaking vacuum of a vacuum plasma system.

The technical advantages and disadvantages of the two forefront plasma spray processes are summarized below:

1. Argon-Shrouded Torch

   a. Benefits:

      (1) It is simple to operate, with relatively low initial cost.

      (2) All operation is carried out in normal, clean workshop.

      (3) Components can be processed in large numbers.

      (4) Torch can give consistent, accurate, and uniform deposits.

      (5) Spraying is in invert atmosphere to give clean, dense coatings.

      (6) Over 95 percent product yield is possible, routinely.

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b. Limitations:

    (1) Relatively short standoff distance requires programmed torch movement to coat complex parts.

    (2) Deposition onto substrates at high temperatures cannot ‚rmally be carried out, because of atmospheric conditions.

2. Low-Pressure or Vacuum Torch

  a. Benefits:

    (1) Components can be preheated without oxidation to minimize internal stress effects and allow low-stress, thick, high-density deposits.

    (2) The plasma jet becomes elongated, allowing larger standoff distances to be used, minimizing the effects of component and torch geometry, and allowing a more complete melt, and denser, more uniform coatings.

    (3) Environmental health and safety problems are eliminated.

  b. Limitations:

    (1) Capital outlay is extremely high.

    (2) Vacuum limits number of parts processed, unless robotic equipment is used.

    (3) High maintenance is caused by powder particles entering pumping system.

    (4) Extra cleanliness is required.

D. HEALTH AND SAFETY

Plasma spray, like numerous other industrial processes being used today, has its hazards, which can be eliminated or minimized with proper awareness and precautions. Potential hazards to workers are dust and fumes, gases, noise, arc radiation, and electrical shock. Dust and fumes produced during plasma arc spraying originate primarily with the material being sprayed. The magnitude of the hazard depends on the material being sprayed and the concentration. A vacuum plasma spray system with robotic control would eliminate these hazards. Other conventional methods are available for worker protection. Most of the materials "oversprayed" are recoverable, leading to no environmental pollution.

The plasma spray process results in the presence of various gases. In addition to the gas being used to form the plasma (argon, helium, nitrogen, hydrogen, etc.), nitrogen oxides of various sorts are produced, as well as ozone from the reaction of atmospheric oxygen and ultraviolet radiation from the plasma arc. Other gases may be present under certain circumstances. For instance, phosgene and dichloroacetyl chloride can be produced by

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reactions in the presence of ultraviolet radiation of the chlorinated hydro-carbons (e.g., trichloroethylene) used for degreasing metal surfaces. Such reactions may occur if spraying is done near degreasing equipment. Precautions should be taken to avoid health problems. Although not toxic, even the inert gases used in the process can cause oxygen depletion in the general area, resulting in a worker becoming unconscious. Few problems will result if proper ventilation is supplied.

Arc radiation has ultraviolet components which can produce temporary or permanent eye damage. The most common eye problem associated with plasma arcs is conjunctivitis, or "arc flash." This is temporary unless reexposure occurs and can be prevented with the use of proper eye protection (Shade 12 or higher). Ultraviolet radiation can also produce skin burns similar to sunburn and just as painful. Heavy work clothing is advisable for mild exposures, and a protective suit is recommended for heavy exposure. Infrared radiation comprises most of the radiation from the plasma arc. Excessive exposure can produce retina burns and cataracts. The precautions listed above can prevent this problem. A plasma arc operated in a vacuum could totally eliminate these hazards.

The noise associated with plasma arc operations may present a hazard because of its intensity or frequency. Noise levels in excess of 90 decibels have been measured near plasma arcs. Also, the noise produced by such arcs is distributed over a wide frequency range, including those to which the ear is sensitive. The effect of noise is a function of the sound intensity, pitch or frequency, and duration. Precautions should be taken to avoid exposure. Noise-attenuation equipment is available for the machines, as well as personal protective equipment for the workers.

Electrical shock hazards from plasma-arc spraying equipment are similar to those presented by other types of electrical equipment. Only well-designed and well-built equipment should be used, and it should be well-maintained. The open-circuit, operating, and supply circuit voltages and amperages are all high enough to present a serious hazard. Proper grounding, insulation, and guarding will minimize electrical shock hazards.

E. ENVIRONMENTAL CONSIDERATIONS

In comparison to chromium electroplating, plasma spray techniques can reduce environmental hazards. Elimination of chromium electroplating removes the requirement for plating tanks, rinse systems, bath maintenance, chromic acid fume removal, or disposal or treatment of hazardous waste. Wastewater is reduced to the IWTP.

Plasma spray of chromium or other materials can reduce the amount of chromium electroplating at a facility. Reductions range from 10 to 80 percent. Each usage would have to be judged on its own merit, based on engineering requirements. Unlike cadmium, chromium is used for varied industrial processes. Materials personnel at each facility would be required to provide technical justifications for each engineering application.

Elimination of plating tanks may be possible if enough chromium electroplating is eliminated. Most facilities already have chrome plating

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tanks; therefore, initial investment would only apply to new facilities, but can be extremely costly. Elimination of the tank will remove ventilation, space, and maintenance requirements for that tank.

Ventilation requirements for a plasma spray system can be much less costly and more efficient in removing chromium. The chief difference is that plating results in chromic acid fumes above the tank that must be removed, while plasma spray generates chromium dust. Chromic acid fumes are corrosive, hazardous to health and safety, and require extensive removal capability. It has been stated that "more chromium goes up the ventilation system than is plated." In some cases, this is true; a great deal of chromium is lost when a recovery system is not used. Plasma spray, on the other hand, has a chromium dust to collect. This dust is much less hazardous, lower in volume, and recoverable. One benefit of removal of a chromic acid tank is that ventilation capability for that system can be applied elsewhere.

Chromium plating is normally accomplished at $130^\circ-140^\circ F$. These temperatures require heating apparatus to maintain tank temperature. Sometimes when a tank is being heavily used, a cooling system is required. Maintaining tank temperature is expensive and energy-intensive. No similar requirement exists for plasma spray.

Chromic acid is highly corrosive. Tanks and equipment need constant maintenance under hazardous conditions. Tanks must be drained, cleaned, and maintained in optimum plating condition. The electrical system supplying the tanks must be maintained in these conditions. Maintenance is very costly depending on the age, material, and man-hour costs of a facility. Under most conditions, plasma will cost less to maintain (excluding vacuum system).

Chromium plating baths use evert anodes (Section I). This results in adding additional chromium to the plating bath to make up for losses through plating, rinsing, and ventilation. Daily monitoring of the plating tank is required and additions are made to maintain chemical balances. This requires trained experienced personnel. Plasma spray will eliminate this need.

If enough plating baths are eliminated, rinse tanks may be eliminated. Many of these tanks run at up to 15 gallons/minute. Elimination of these tanks eliminates the need for treatment of approximately 7-8 million gallons of wastewater/year and can save several hundred thousand dollars in treatment and disposal costs, as well as elimination of future liabilities. Treatment facilities can also be designed for lower flow rates.

Although savings may be significant, the initial cost of changing chromium electroplating for plasma spray is important. Extensive testing of parts would be required, initial costs for advanced equipment could be high, and training personnel would require funds. These costs might be justified if all chromium treatment could be eliminated, or if a facility was having difficulty in meeting discharge limits. In most cases, however, chromium cannot be entirely eliminated from the discharge to sewer, and chromium plating cannot be eliminated. This means treatment for chromium would still be a requirement.

Chromic acid is used for stripping, conversion coatings, chromate-phosphate treatments, anodizing, plating, etc. Chromium is found in paint-stripping wastes, machine shop wastewater, engine cleaning wastewater, etc. Elimination of chromium plating would not eliminate requirements for chromium treatment. Similar chemical usage would result since the pH for the entire waste stream would still require adjustment. SO_2 or other reducing chemical cost changes would be minimal. The major savings would result from elimination of batch treatments of concentrated chromium solutions and reduction of wastewater volumes.

Wastewater volumes can be eliminated without elimination of chromium electroplating. With controlled rinsing, water usage can be made to match evaporation rates out of the plating tanks. This allows all rinsewater to be returned to the plating tank, eliminating treatment requirements. Similarly, condensed chromic acid from ventilation can be returned to the plating tank. Extensive work has been completed by the Navy under the title of "Innovative Hard Chrome Electroplating," which eliminates discharge of chromium from chromium electroplating operations to industrial wastewater treatment operations.

F. RECOMMENDED RESEARCH PROGRAM

The probability of complete elimination of chromium electroplating by plasma spray techniques at the present time is minimal. Elimination of the most chromium electroplating would probably require state-of-the-art auto-mated vacuum plasma spray equipment with laser remelt. This equipment would require high initial costs with high maintenance. Evaluations would require large amounts of parts testing and materials evaluation at high costs.

Much plasma spray research is being done by the civilian community. Much of the advanced work, which has the greatest probability of eliminating chromium electroplating, is still in preliminary stages. Development is pro-ceeding rapidly, with a great deal of knowledge becoming available each year.

The elimination of chromium electroplating will not eliminate chromium discharges from the electroplating shop, nor from other shops. Treatment and disposal of chromium wastes will still be required. Much of the cost of this treatment is based on volume of water, not chromium content.

Some methods are available for minimizing and eliminating rinsewater and chromium discharges from chromium electroplating operations. The Navy has developed and implemented O-discharge systems. These methods should be applicable to Air Force facilities.

Minimal research is recommended for replacement of chromium electro-plating by plasma spray. Economic benefits, based solely on environmental considerations, do not appear substantial enough to warrant large government research efforts. The following is recommended.

1. Evaluate the extent of liabilities from chromium wastes at each facility. Does the facility have a problem? If so, what is the extent of the problem and what are the economics involved?

2. Upon determination of a problem of significant economic stature, evaluate the impact of elimination of chromium discharges from the chromium electroplating processes. Compare the technical and economic advantages of each system, and choose the appropriate technology.

3. Concurrent technical evaluation of parts that can be immediately changed to a plasma spray process to replace chromium electroplating should be conducted. This study should be based on past justifications of similar parts. The impact of replacing the process on those parts should be determined in relation to possible reduction in the number of chromium electroplating tanks.

G. COST ESTIMATE

Based on anticipated minimal impact of elimination of chromium electroplating on environmental problems, no funding is recommended for research at HQ AFESC.

H. SUMMARY

Plasma spray has developed into a viable multipurpose industrial process since its conception in the 1920s. A high-temperature (up to 40,000°C) plasma gas melts and transports materials at high velocities to impact on the surface to be coated. New techniques such as automated vacuum plasma spraying, inverted gas shielding, and laser remelting make it possible to minimize or eliminate some of the major problems associated with plasma spray, including high-oxide deposits, poor adhesion, low densities, and high residual stresses.

Some benefits of plasma spray are reduced health and safety problems, elimination of hazardous waste production, and reduction of ventilation requirements. There is no discharge to sewers of chromium-contaminated wastewaters. Powdered chromium is removed from the air by a filter system less demanding than those necessary for chromium electroplating. There are no hazardous acids or chemicals to work with reducing health and safety problems. Replacement of chromium electroplating by plasma spray would be beneficial for environmental health and safety reasons.

Chromium is found in many processes throughout the ALCs. Chromium :- paint stripping, machining, and plating processes finds its way to the industrial waste plant or to barrels of concentrated hazardous waste. These wastes need to be treated or disposed of. Chromium treatment cannot be eliminated just by elimination or reduction of chromium electroplating. 0-discharge system may be able to eliminate most chromium from chromium electroplating from reaching the sewers.

Plasma spray techniques are estimated to be able to replace 10-80 percent of chromium electroplating. Indications are that, on the average, a minimal amount of chromium electroplating can be replaced. It is recommended that minimal research effort be applied to modification of plasma spray, unless environmental considerations at a particular installation require elimination of chromium electroplating. The effort should be limited to technical justification of process change due to past records for parts previously plasma-sprayed. If enough parts can be plasma sprayed, then the

number of plating tanks should be reduced or eliminated. The remaining tanks should be converted to a closed-loop system, eliminating rinsewater and scrubber discharges. The closed-loop systems are not the subject of this report, but they are easily modified for each facility.

SECTION VI

NICKEL BORON AS A REPLACEMENT FOR CHROMIUM ELECTROPLATING

A. INTRODUCTION TO NICKEL BORON

Nickel boron is a electroless nickel process using boron containing
reducing agents, especially the borohydrides and amine boranes. Deposits
are characterized by uniform deposition, relative hardness, solderability,
and electrical conductivity. These characteristics make nickel boron
idei 'y suited for applications in the electronics industry.

Components of the electroless bath include an aqueous solution of metal
ions, catalyst, reducing agent, complexing agents, and bath stabilizers
operating in a specific metal ion concentration, temperature, and pH range.
Unlike conventional electroplating, no electrical current is required for
deposition. The base substrate must be catalytic in nature.

The electroless bath provides a deposit which follows all contours of
the substrate exactly, without buildup of corners or edges. A sharp edge
receives the same thickness as a "blind hole." If air or evolved gases are
trapped in a blind hole or on a downward-facing cavity, however, this will
prevent deposit in these areas.

When a proper catalytic surface is introduced into the electroless
nickel bath, a uniform deposition begins. Minute amounts of the electroless
metal itself can catalyze the reaction, so the deposition is autocatalytic
after the original surfaces are coated. Electroless deposition continues,
providing that the metal ion and reducing agent are replenished. Metal ions
are reduced to metal by the action of chemical reducing agents, which donate
electrons. The metal ions accept the electrons and react with the electron
closers. The catalyst accelerates the reaction, allowing oxidation of the
reducing agent.

The plating bath must be monitored and controlled closely to maintain
proper ratios and chemical balance. The deposition rate depends on control
of temperature, pH, and metal ion/reducer concentration. Complexing agents
act as buffers to help control pH and "free" metal salt ions. The
stabilizers act as catalytic inhibitors, retarding potential spontaneous
decomposition of the bath. Impurities, inorganic ions, and organic
contamination in the bath will affect deposition properties and appearance,
causing roughness, porosity, hardness, color, and adhesion changes.

B. PROCESS DESCRIPTION

Research to develop alternative reducing agents leads to investigation
of boron containing reducing agents; in particular, the borohydrides and
amine boranes. The borohydride reducing agent may consist of any water-
soluble borohydride. Sodium or potassium borohydride is generally
preferred. The pH of the solution must be between 12.0-14.0 to suppress
formation of nickel boride and allow formation of elemental nickel. To
prevent precipitation of nickel hydroxide, ligands are used. Strong
complexing agents are used and cause decreased rate of deposition. Constant
additions of ammonia hydroxide are required, since the pH decrease is due to

the reduction reaction. The operating temperature is 90-100°C. Deposits are 94-97 percent nickel. The baths can produce deposited hardnesses of 650 to 750 VHN or, after heat treatment at 400°C for 1 hour, hardnesses of 1200 VHN. The melting point of the deposits is 1080°C. The difficulties encountered in operating this solution outweigh the advantages for most applications. Acid nickel solutions are most commonly used.

Deposits of similar composition are obtained from electroless nickel solutions using amine borane as the reducing agent. These solutions provide a wide range of operating conditions and control of the resulting deposits. Commercial applications are generally limited to N-dimethylamine borane (DMAB), used primarily in the United States, or N-diethylamine borane (DEAB), used primarily in Europe. DMAB is readily soluble in water, while DEAB requires ethanol or another short chain aliphatic alcohol to enhance solubility. Table 15 shows a typical sodium borohydride electroless nickel bath.

These acid nickel boron solutions deposit 96-99 percent nickel by weight. pH is maintained between 4.8 and 7.5, with an operating temperature range of 65-77°C. The deposits have a very high melting temperature of 1350°C. Baths with less than 1 percent boron have excellent solderability and good ultrasonic bonding characteristics.

TABLE 15. NICKEL BORON BATH COMPOSITION

Typical Sodium Borohydride Electroless Nickel Bath		Typical DMAC Electroless Nickel Bath	
Nickel Chloride	31 g/L	Nickel Sulfate	15 g/L
Sodium Hydroxide	42 g/L	Sodium Acetate	15 g/L
Ethylenediamine, 98%	52 g/L	DMAB	4 g/L
Sodium Borohydride	1.2 g/L	Lead Acetate	.002 g/L
Thallium Nitrate	.022 g/L	pH	5.9
pH	14	Temperature	26°C
Temperature	93-95°C		

C. PRODUCT APPLICATIONS

Most applications of nickel boron are associated with the electronics field. Lower-temperature nickel boron systems can easily be applied to plastics. Deposition is uniform in all systems. Generally, nickel boron solutions can be used for engineering requirements for uniform deposit, hardness, solderability, diode bonding, electrical conductivity, rhodium replacement, and gold replacement in the electronics industry.

In comparison to chromium electroplating, nickel boron baths are much more sensitive to contamination. Nickel boron deposition tensity stress can become excessive, causing poor adhesion. This is especially true for heavier buildups. Plating rates are greater for nickel boron, but bath temperatures are generally higher, requiring higher energy requirements. Corrosion resistance is less because of porosity of deposit of nickel boron. Overall, chromium plating is much cheaper and easier to operate. Buildup of many

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parts would be impossible due to increased porosity with greater thicknesses, adherence, and stress problems.

Nickel boron can replace some applications of hard chrome plating, but usually not enough to make a significant difference in chromium plating tank requirements, or in chromium content of ITWP influent. Since nickel boron baths are much more sensitive to contamination, return of rinsewater to the plating bath would not be practical with chromium. Overall, the potential for nickel boron as a replacement for hard chromium is extremely low.

D. _ SARCH REQUIREMENTS

As the potential for nickel boron plating as a replacement for hard chrome plating is low, replacement would be a negligible contribution to environmental improvements (with possibility of det..mental effects); further research is not recommended. The materials engineer of each facility should determine if nickel boron offers any significant engineering advantage over a chromium coating. If so, this engineer must determine if there are enough applications to justify changing a plating tank from chromium to nickel boron.

E. COST ESTIMATE

Year 1	Year 2	Year 3
—	—	—

F. SUMMARY

Several characteristics make nickel boron an unlikely candidate for most chromium electroplating applications. Chemical costs and extensive bath maintenance programs (caused by sensitivity of baths to contaminants) make nickel boron baths expensive. When heavy buildup is required, excessive tensile stress can develop, causing poor adhesion. Corrosion resistance is usually less than for chromium because of porosity. Energy requirements are much greater because of higher bath temperatures 90–100°C.

Nickel boron can replace some applications of hard chromium electroplating, but in most cases, not enough to significantly affect tank requirements or environmental problems associated with chromium electroplating. With baths much more sensitive to contamination, return of rinsewater to the plating bath would not be practical, as with chromium electroplating. Overall, the potential of nickel boron as a replacement for hard chromium electroplating is extremely low. No significant research is recommended.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

A. CONCULSIONS

1. Ion Vapor Deposition (IVD) Of Aluminum To Replace Cadmium Electroplating

IVD is a technique wherein the material to be used as a coating is evaporated within a vacuum chamber, then condensed on the part being coated. The process is distinguished from other vacuum deposition techniques by a glow-discharge cleaning process, and by plating on all sides, applying current to make the "part" cathodic.

IVD aluminum is a soft ductile coating of pure aluminum. Performance advantages of IVD or aluminum over cadmium electroplating have been confirmed over the past decade. Numerous tests have been conducted by McDonnell Douglas, the Navy, and the Air Force. Tests have been conducted on fasteners, steel panels, engine parts, etc., and all have shown superior corrosion resistance. Specific attributes of IVD aluminum include:

    a. It outperforms cadmium and other coatings in actual service tests.

    b. It has a useful temperature to $925^{\circ}F$ ($496^{\circ}C$).

    c. It can protect steels of all strength levels because there is no hydrogen embrittlement.

    d. It does not cause solid metal embrittlement of Titanium.

    e. It can be used in contact with fuel.

    f. It provides galvanic protection to aluminum alloys and does not cause fatigue reduction.

    g. It can be applied thinner than alclad on aluminum alloys. This results in weight savings. It is not limited to rolled forms.

    h. It provides man-hours on EMI shielding, when used, instead of electrical connectors.

    i. Neither the process nor the coating involve toxic materials.

IVD aluminum is equal or superior to cadmium electroplating for all engineering applications in use by the aerospace industry. Production equipment is available.

2. Noncyanide Strippers As A Substitute For Cyanide Strippers

Cyanides are dangerous to health and environment. Cyanide strippers contribute to the cyanide wastes which reach the IWTP by way of wastewater. These must be treated, usually by alkaline chlorination. These strippers

have been used to remove various plated metals from substrate metals. These solutions and the wastewater resulting from them are difficult to treat because stable ferrocyanides and other cyanide complexes are not amenable to chlorination. Since facilities usually have a total cyanide limit, they may have trouble avoiding outages.

Over the years, regulatory pressures have resulted in development of many noncyanide stripping baths. Most of the work is being completed and marketed by the private sector to DOD. Use of the baths throughout DOD is usually the prerogative of the individual commands. Each electroplating shop has its own stripping processes. Noncyanide baths have been tested throughout DOD and could be used to replace all cyanide strippers in use by the ALCs.

With the elimination of cadmium electroplating and cyanide strippers, most of the cyanide would be eliminated from the plating shop. The small contributions by usage areas such as silver plating, or copper plating, can then be eliminated by process changes readily available today. The total elimination of cadmium and cyanide is therefore feasible with present technology.

3. Plasma Spray Of Chromium As A Substitute For Chromium Electroplating

Plasma spray is one of the many thermal spray processes. Since its introduction in the 1950s, it has developed into a viable engineering process. The list of materials being applied is constantly growing, as is the number of applications. Extremely high temperatures in a plasma gun allow any material to be sprayed, provided: (1) it melts without significant disassociation, and (2) that a practical temperature interval exists between melting and boiling points.

Past problems have been related to burning of substrate, poor adhesion, and porosity. Methods are available which will reduce or eliminate most of these problems. New methods, such as laser processing and vacuum plasma spray techniques, are reliable in eliminating adhesion and porosity problems. Vacuum plasma spray can also reduce the oxide deposited. Proper parameter control can eliminate most other problems.

Plasma spray of chromium is a viable engineering alternative to many chromium-plated parts. The specific engineering properties desired for each part would determine if plasma spray could be used. Many proprietary materials and equipment are on the market, with constant competitive research occurring in the private sector. This research makes it unlikely that the Air Force needs to contribute to development.

In evaluating the potential for replacing chromium electroplating at each facility with plasma spray, the facility needs to determine if enough chromium plating can be eliminated to remove a plating tank(s). If so, it may be worthwhile to implement the plasma spray. During evaluation, one must remember that other major sources of chromium (paint stripping processes, chromating, etc.) will prevent elimination of chromium metal treatment of wastewater. Chemical savings can be achieved, but the wastewater must be raised and lowered in pH, regardless of chromium content.

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4. Nickel Boron Plating As An Alternative to Chromium Plating

Nickel boron is an electroless nickel process where boron is co-deposited with the nickel, rather than the usual phosphorous. The amount of boron varies with application. The characteristics associated with nickel boron are its resistance to high temperatures (1300-1400° melting point C ., purity of deposit (to 99.99 percent), hardness and wear resistance (Rockwell C69-70), and solderability (solders with mild flux, months after plating). Because of these characteristics, nickel boron has its major application in the electronics industry. Excellent solderability and electrical conduction make nickel boron a viable gold replacement.

Several disadvantages of the system relative to chromium electroplating are porosity, expense, low corrosion resistance, and a bath contamination. This high porosity gives less corrosion protection than the standard electroless nickel baths, or chromium plating. With bath contamination, deposition tensile stress can become excessive, causing poor adhesion. The bath plates at one-third to one-half the rate of a phosphorous electroless nickel bath. The cost is 10-15 times that of a standard nickel phosphorous bath. Also, to obtain high hardness characteristics, an added heat-treat step is necessary.

Replacement of chromium in certain specific applications may be practical, but overall replacement is not feasible. An added plating tank with limited use and added cost would result. It is not recommended for extensive research. Each ALC materials laboratory should determine if there is an application.

NOTE: Techniques are available to eliminate chromium discharge from chromium electroplating, without eliminating the process. The Navy has developed "Innovative Hard Chromium Electroplating" that can eliminate chromium wastes.

E. RECOMMENDATIONS

Upon evaluation of the specified processes, the following recommendations are made by HQ AFESC/RDVS:

1. Ion Vapor Deposition of Aluminum as a Replacement of Chromium. Recommend this process be substituted for cadmium electroplating. Suggest funding of project to (a) develop a database to provide technical justification for process and technical order changes, (b) develop a test plan to provide testing and evaluation of parts not immediately justifiable, (c) provide demonstration site for complete elimination of cadmium, and (d) eliminate cadmium plating from all ALCs.

2. Replacement of Cyanide Strippers with Noncyanide Strippers. Recommend funding a study of noncyanide stripping processes and applications used throughout DOD and industry. Recommend changes to proven noncyanide stripping baths as the study provides technical justification.

3. Plasma Spray of Chromium as a Replacement for Chromium Plating. Recommend each ALC consult with materials personnel to determine each

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specific application that plasma spray can be replaced. If enough applications exist to eliminate one or more plating tanks, then replacement should be made.

4. Nickel Boron as a Replacement for Chromium Electroplating. Recommend no change to nickel boron except for limited applications where superior performance of coating is needed.

F. ESTIMATED COSTS

The following estimates are supplied for research requirements of the subject processes.

Application	Costs		
	YR 1	YR 2	YR 3
1. Ion vapor deposition of aluminum	400K	850K	500K
2. Noncyanide Strippers	300k	500k	200k
3. Plasma Spray	–	–	–
4. Nickel Boron Electroplating	–	–	–

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